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potash, giving a substance which crystallised from alcohol in colourless, microscopic needles, m. p. 216—217° (Found: C, 70·4; H, 6·0; N, 7·7. $C_{23}H_{22}O_4N_2$ requires C, 70·8; H, 5·6; N, 7·2%). The isomerides were not affected by boiling dilute sulphuric acid, but when a solution of either in concentrated sulphuric acid was kept for ½ hour and poured into water, benzoic and mandelic acids, benzaldehyde and ammonia were formed. This reaction, in conjunction with the action of alcoholic potash upon the isomerides of m. p.'s 250—251° and 223—224°, shows that these substances are isomeric forms of *benzylidenebisbenzoylmandelamide*,

$$(OBz{\cdot}CHPh{\cdot}CO{\cdot}NH)_2CHPh.$$

This structure was confirmed by the isolation of a small quantity of the higher-melting isomeride (identity determined by the mixed melting-point method) from the product of the fusion of benzoylmandelamide (excess) and benzaldehyde at 140—160° for 2 hours.

The production of similar substances has been recorded—ethylidenedibenzamide (Hepp and Spiess, *Ber.*, 1876, **9**, 1425); benzylidenebisacetylmandelamide (Japp and Knox, *loc. cit.*).

Action of Hydrogen Chloride upon Benzoylmandelonitrile.—Hydrogen chloride, dried by sulphuric acid, was passed for about 20 hours through a dry, cooled, ethereal solution of benzoylmandelonitrile, protected from atmospheric moisture. On removal of the ether, a clear, viscous, amber-coloured oil remained which would not solidify, and gave benzoylmandelamide when boiled with 10% aqueous alcohol for 2 hours.

When moisture was not excluded during the reaction, much benzoylmandelamide was produced. After several crystallisations from alcohol, it was obtained as a colourless, microcrystalline mass, m. p. 160—161° (Found: C, 70·4; H, 5·8. Calc. for $C_{15}H_{13}O_3N$: C, 70·6; H, 5·1%) (compare Orton, J., 1901, **79**, 1354).

Condensation of Acetaldehydecyanohydrin and Benzaldehyde.—When these substances were condensed by hydrogen chloride in ethereal solution, lactobenzylideneamide, m. p. 132° (Found: C, 67·5; H, 6·5. Calc. for $C_{10}H_{11}O_2N$: C, 67·8; H, 6·2%), was formed, but no 2-phenyl-5-methyloxazole could be detected (compare Fischer, *loc. cit.*).

Condensation of Anisaldehydecyanohydrin and Anisaldehyde.—Minovici studied the action of hydrogen chloride upon anisaldehydecyanohydrin in ethereal solution alone (*Ber.*, 1899, **32**, 2206) and in the presence of anisaldehyde (*Ber.*, 1896, **29**, 2097) and obtained in each case a white, crystalline substance, $C_{17}H_{15}O_3N$, m. p. 145°. In the latter case he described it as 2 : 5-dianisyloxazole, but in the former he assigned to it the constitution $OMe{\cdot}C_6H_4{\cdot}CH(CN){\cdot}CO{\cdot}C_6H_4{\cdot}OMe$

without giving any evidence for his conclusion. When his experiments were repeated, 2 : 5-dianisyloxazole, m. p. 143—144°, was isolated in each case (Found: C, 72·8; H, 5·6. Calc.: C, 72·6; H, 5·3%). The picrate was obtained in yellow needles, m. p. 214—216°, after one crystallisation from acetone.

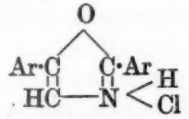
Condensation of m-*Nitrobenzaldehydecyanohydrin and* m-*Nitrobenzaldehyde.*—This condensation was performed similarly to the preceding ones; it was necessary, however, to add some benzene to the ether to bring the aldehyde into solution. (Such addition was necessary in the succeeding condensations also.) The yellow reaction product was extracted for several hours with alcohol. The sparingly soluble substance (*A*) that separated from the extract was obtained as a canary-yellow, microcrystalline mass, m. p. 277—278°, after recrystallisation from glacial acetic acid (Found: C, 56·8; 56·8; H, 3·5, 3·6%). The residue from the extraction was separated by fractional crystallisation from acetic acid into a less soluble substance, m. p. 238° (Found: C, 57·9; H, 2·9. $C_{15}H_9O_5N_3$ requires C, 57·9; H, 2·9%), and a more soluble one, m. p. 225—227° (Found: C, 57·8; H, 3·2%). Since the latter remained unchanged in melting point after recrystallisation from acetic acid and from nitrobenzene, these two substances are regarded as isomeric forms of 2 : 5-*di*-m-*nitrophenyloxazole.*

Condensation of m-*Nitrobenzaldehydecyanohydrin and Benzaldehyde.*—The crude product contained a substance which, after four crystallisations from alcohol, was obtained in cream-coloured needles, m. p. 156—157°, and is probably 2-*phenyl*-5-m-*nitrophenyloxazole* (Found: C, 67·2; H, 3·9. $C_{15}H_{10}O_3N_2$ requires C, 67·7; H, 3·7%). A considerable quantity of the substance (*A*), m. p. 277—278° (see preceding experiment), was isolated from the crude product. That it is produced from the *m*-nitrobenzaldehydecyanohydrin only was proved by the following experiment.

Action of Hydrogen Chloride upon m-*Nitrobenzaldehydecyanohydrin.*—The action of hydrogen chloride upon an ether–benzene solution of this cyanohydrin produced a pale yellow substance which, when dried over paraffin wax and solid sodium hydroxide, contained ionic chlorine and melted at 95—99° (decomp.). When a methyl- or ethyl-alcoholic solution of it was kept or boiled, a precipitate formed rapidly. This precipitate, on purification, yielded a substance, m. p. 277—278°, identical with the substance (*A*), and much ammonium chloride and 2 : 5-di-*m*-nitrophenyloxazole were found in the mother-liquor. It seems probable, therefore, that the following reactions took place during the passage of hydrogen chloride into the cyanohydrin solution (Ar = $NO_2 \cdot C_6H_4$),

$$Ar\cdot CH(OH)\cdot CN \xrightarrow{HCl} \begin{cases} Ar\cdot CH(OH)\cdot CCl{:}NH,HCl \\ Ar\cdot CHO + HCN \end{cases}$$

$$Ar\cdot CH(OH)\cdot CCl{:}NH + Ar\cdot CHO \longrightarrow$$



$$HCN \xrightarrow{HCl} H\cdot CCl{:}NH,HCl \xrightarrow{H_2O} H\cdot CO_2H + NH_4Cl + HCl$$

and that on boiling the crude product with alcohol (or water) the following reactions occurred :

$$Ar\cdot CH(OH)\cdot CCl{:}NH,HCl \rightarrow \begin{cases} C_{16}H_{10}O_5N_4 + HCl + H_2O \\ Ar\cdot CH(OH)\cdot CN + HCl \end{cases}$$

The similarity in the methods of preparation and in properties of the substance (*A*) and the compound obtained by Japp and Knox and by Minovici from benzaldehydecyanohydrin, makes it highly probable that they have similar structures. The substance (*A*) (Found : C, 56·8; H, 3·5. $C_{16}H_{10}O_5N_4$ requires C, 56·8; H, 3·0%) is therefore considered to be 3-*keto*-2 : 5-*di*-m-*nitrophenyl*-3 : 4-*dihydro*-1 : 4-*diazine*. Its colour is slowly changed from canary-yellow to moderately deep brown by light. When the diazine was treated with chromic and acetic acids, 80% of it was recovered unchanged and no trace of the remainder could be found.

Condensation of p-*Nitrobenzaldehydecyanohydrin and* p-*Nitrobenzaldehyde*.—This condensation was performed similarly to that of the *m*-isomeride, and 3-*keto*-2 : 5-*di*-p-*nitrophenyl*-3 : 4-*dihydro*-1 : 4-*diazine* was obtained as a canary-yellow, microcrystalline mass, m. p. 332—334° (Found : C, 56·9; H, 3·3. $C_{16}H_{10}O_5N_4$ requires C, 56·8; H, 3·0%), by extraction of the crude product twice with alcohol and crystallisation of the residue twice from acetic acid and once from nitrobenzene.

All the various residues were mixed together and, after removal of the solvents, the product was extracted several times with alcohol and finally crystallised from alcohol and from acetone, golden-yellow, microscopic needles of 2 : 5-*di*-p-*nitrophenyloxazole*, m. p. 228—232°, being obtained (Found : C, 58·4; H, 3·3. $C_{15}H_9O_5N_3$ requires C, 57·9; H, 2·9%).

Attempted Hydrolysis of "Minovici's Compound."—The compound was heated with concentrated hydrochloric acid (20 parts) in a sealed tube at 200° for 21 hours, and was converted thereby merely into its hydrochloride.

The author is indebted to Dr. H. Stephen for suggesting the subject of the research, and for valuable advice connected therewith, and also to the Chemical Society for a grant towards its cost.

THE UNIVERSITY, MANCHESTER. [*Received, January 20th*, 1927.]

CV.—*Studies in the Composition of Coal. The Resolution of Coal by Means of Solvents.*

By CHARLES COCKRAM and RICHARD VERNON WHEELER.

As the result of systematic researches initiated in 1912, which have followed since 1915 the scheme outlined by Stopes and Wheeler (*Rep. Brit. Assoc.*, 1916), we can now express the " analysis " of a coal in a form which indicates its properties more clearly than the usual " proximate " and " ultimate " analyses. For example, the characters of the four component bands of the Hamstead coal, a markedly banded bituminous coal, can be expressed in the following manner :

	Per cent. by weight.			
	Ulmin compounds.	Organised plant entities.	Hydrocarbons and resins.	General character of plant entities.
Vitrain	96	Nil.	4	—
Clarain	92	5	3	Cuticles and spore exines.
Durain	83	15	2	Cuticles, spore exines, and woody tissues.
Fusain	20	80	Nil.	Woody tissues.

In these analyses, certain resin-like compounds, which cannot be definitely classed as resins, present in the coals in small quantity, have been ignored.

Other researches have dealt, and are dealing, with the constitution of the ulmin compounds and the organised plant entities (see, *e.g.*, Tideswell and Wheeler, J., 1922, **121**, 2345; Legg and Wheeler, J., 1925, **127**, 1412; Francis and Wheeler, *ibid.*, p. 2236). The present research is concerned with that portion of a normal bituminous coal which can be extracted by organic solvents, the sometimes incorrectly named " resinous " portion.

In many bituminous coals there are inclusions of resinous matter, usually on the cleavage planes, which can be separated mechanically and are thus readily examined (see Wigginton, *Fuel*, 1926, **5**, 476). With these we are not at present concerned. The substances extractable from a normal bituminous coal by organic solvents presumably contain the remains of oils, fats, and waxes of the original coal-forming plants, in addition to resins and their degradation products disseminated throughout the coal mass, such as the

microscopic rods preserved *in situ* in what are known to have been resin-containing cells (see White and Thiessen, *U.S. Bureau of Mines*, Bull. 38, 1913; Francis and Wheeler, J., 1926, 1410). All such substances, although they could not have formed more than a small proportion of the plants of coal-measure times, would yet, owing to their resistance to decay, survive and proportionately increase in amount while the plant material was accumulating and partly decaying in the early stages of coal formation.

Although this "resinous" portion forms but a small fraction of a bituminous coal, it is an important constituent technically, by reason of the properties it confers on the coal; and it is of considerable scientific interest in relation to the origin, mode of formation, and constitution of coal.

A critical survey of the more important work carried out before 1918 on the action of solvents on coal has been given by Stopes and Wheeler in their monograph "The Constitution of Coal" (London, 1918), reprinted, with additions by Dr. F. V. Tideswell bringing it up to date, in "Fuel in Science and Practice," Vol. III, 1924. Therein the value of pyridine, first suggested by Bedson (*Trans. Inst. Min. Eng.*, 1899, **16**, 388) as a means of resolving the coal conglomerate, was emphasised. Clark and Wheeler had found (J., 1913, **103**, 1704) that when the pyridine extract of a bituminous coal was treated with chloroform or benzene, up to 10% (on the original coal) dissolved. This fraction, soluble in both pyridine and chloroform, differed markedly in properties from the bulk of the coal, and from a consideration of those properties Clark and Wheeler concluded that their treatment had made "a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated" (*loc. cit.*, p. 1706). The portions of a bituminous coal (α), insoluble in pyridine, and (β), soluble in pyridine but insoluble in chloroform or benzene, were found to be of the same type, differing mainly in their behaviour towards pyridine, whilst both were quite distinct from (γ), the portion soluble in both pyridine and chloroform. Clark and Wheeler had termed the fractions (α) and (β) "cellulosic" or, alternatively, in conformity with a nomenclature used by Lewes (*J. Roy. Soc. Arts*, 1911, **60**, 135), "humic" compounds. Stopes and Wheeler (*loc. cit.*, p. 41) pointed out that, until the composition of these groups of compounds had been more definitely ascertained, it was desirable to use less dogmatic terms than "cellulosic" and "resinic," and proposed the non-committal labels α, β, and γ, which are now commonly used.

Jones and Wheeler (J., 1916, **109**, 707) summarised the in-

formation then available regarding the γ-compounds, which they considered to be derived mainly from the gums, resins, and starches of the original coal-forming plants. They are clearly a mixture of several classes of compounds. Jones and Wheeler (J., 1914, **105**, 140) had obtained from them, by the solvent action of pentane, crystals of paraffin wax (heptacosane), m. p. 55—59°, amounting to 0·10% on the original coal. We have now attempted further to resolve the mixture into simpler components by suitable solvents.

Experimental.

The γ-Compounds.—Supplies of the γ-compounds from the different coals were obtained by extraction with pyridine at its boiling point, followed by treatment of the extract with boiling chloroform. The action of pyridine on coal is often regarded as that of a reagent rather than a solvent. Harger (*J. Soc. Chem. Ind.*, 1914, **33**, 389) appears to have been the first to suggest that it effects "a process similar to depolymerisation." This view, for which no evidence has been adduced, has been adopted by later workers, notably by Illingworth ("Researches on the Constitution of Coal," London, 1921), but cogent reasons for rejecting it have been advanced by Tideswell (*Fuel*, 1922, **1**, 246). The work of Pearson (*J. Soc. Chem. Ind.*, 1923, **42**, 241) supports the view that pyridine is a solvent which resolves mechanically the colloidal mass of coal.

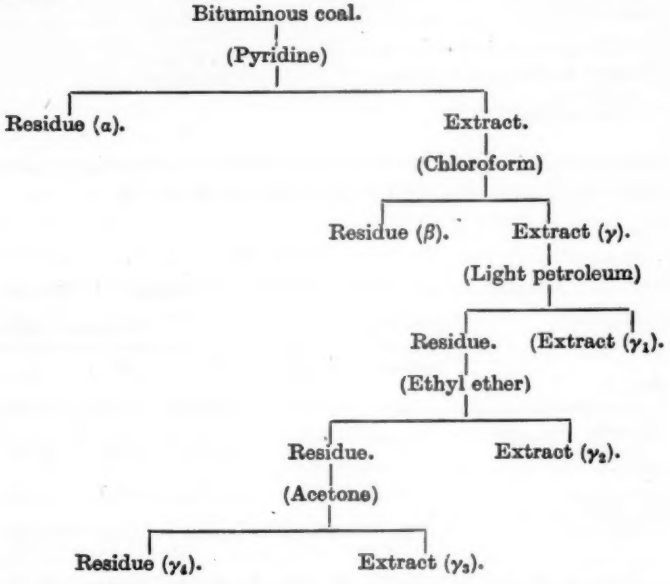
The first resolution of the coals in this research was by pure dry pyridine. The coals, dried and ground to pass a 10- and remain on a 60-mesh sieve, were extracted in large Soxhlet apparatus of special design. These and all subsequent extractions were carried out in an atmosphere of nitrogen. When extraction was complete, the solution was concentrated on a glycerol-bath and poured into a mixture of equal parts of concentrated hydrochloric acid and water. The mixed β- and γ-compounds were precipitated as a dark brown powder. This was filtered off, washed with dilute acid and with hot water, purified by steam distillation, and dried in a vacuum at 100°. In this way all but a trace of pyridine was removed.

The extraction of the γ-compounds by chloroform was completed in from 10 to 14 days. After removal of the solvent, the extracts were obtained as reddish-brown, brittle solids, m. p. 95—100°.

Resolution of the γ-Compounds.—In preliminary tests to determine the most suitable solvents with which to effect the resolution of the γ-compounds, acetone, ethyl ether, and light petroleum were found to be the most satisfactory. Ethyl alcohol tended to produce colloidal dispersion and therefore was not used.

With the particular sample of γ-compounds used in the preliminary experiments, acetone dissolved 85—90%, ethyl ether 70%, and light

petroleum 33%. In the scheme of resolution finally adopted, the least effective solvent, light petroleum, was used first, the residue was extracted with ether, and any material then remaining was treated with acetone. The full scheme of resolution of the coals was as follows :



The fractions so obtained have distinctive properties, shortly to be described, which enable a judgment to be formed as to the character and origin of the groups of compounds each contains. We have made no attempt to isolate pure compounds, since a comprehensive research with this end in view is being carried out on a coal from Upper Silesia by Hofmann and Damm (see preliminary account, *Brennstoff-Chem.*, 1922, **3**, 73; 1923, **4**, 65).

In conformity with the nomenclature introduced by Stopes and Wheeler, the several fractions of the γ-compounds have been labelled, for convenience in reference, γ_1, γ_2, γ_3, and γ_4. A large number of bituminous coals have been resolved according to this scheme. In each instance the respective fractions have the same characteristics. It will therefore suffice here to record the results of examination by these means of one coal, a typical South Yorkshire coking coal from the Parkgate seam. This will be referred to as Parkgate A. The clarain portion only of the seam was examined. Its analysis is recorded in Table I.

By treatment with pyridine and chloroform, the proportions of α-, β-, and γ-compounds obtained were 75·8, 17·3, and 6·9%,

TABLE I.

Analysis of Parkgate A Clarain.

Proximate.		Ultimate.	
		Per cent. on ash-free, dry coal.	
Moisture	3·18%	Carbon	83·60
Ash	1·23%	Hydrogen	5·46
Per cent. on ash-free, dry coal.		Oxygen	6·75
Volatile matter, other than moisture	38·83	Nitrogen	1·72
"Fixed carbon"	61·17	Sulphur	2·47

respectively. Further resolution of the γ-compounds, in the manner described, gave the results recorded in Table II.

TABLE II.

Resolution of γ-Compounds. Parkgate A Clarain.

	% of total γ-compounds.	% of coal.	Ultimate analysis. C.	H.	S.	O + N.
Soluble in light petroleum (γ_1)	33	2·30	83·90%	9·00%	0·74%	6·36%
Soluble in ethyl ether (γ_2)	37	2·54	82·72	6·90	0·91	9·47
Soluble in acetone (γ_3)	12	0·83	79·00	5·70	0·89	14·41
Insoluble in acetone (γ_4)	18	1·23	80·00	5·90	1·10	13·00

The nitrogen contents of the fractions were not determined quantitatively, since minute traces of pyridine were sometimes retained by them. Each fraction could be completely redissolved in the cold solvent.

Examination of Fraction γ_1.—Extraction of the γ-compounds with light petroleum was completed in 14 days. The extract removed during the first few hours consisted entirely of hydrocarbons. As the extraction approached completion, the extract became darker in colour owing to the solution of some resinous matter. The total extract was a white, crystalline substance mixed with a certain amount of red oil. On drying in a vacuum, a reddish-brown material of the consistency of vaseline, mobile at temperatures above 80°, was obtained. On dissolving this material in ether and washing successively with dilute acid and alkali, traces of bases and fatty acids (volatile in steam) were obtained.

The remainder of the oxygenated compounds, forming 20% of the γ_1-fraction, were separated by Robinson's method (J., 1925, **127**, 768). They were resinous, dark red compounds, m. p. 90—95°, free from nitrogen and sulphur, completely soluble in cold chloroform, and of composition : C, 84·21; H, 7·31; O, 8·48%.

The rest of the γ_1-fraction consisted of saturated and unsaturated hydrocarbons in nearly equal amounts, and was similar to the neutral oils investigated by Hofmann and Damm (*loc. cit.*). The saturated hydrocarbons were obtained as a light yellow, faintly fluorescent oil having the characteristic odour of paraffins. Analysis gave: C, 87·4; H, 11·13; O, 1·47%, showing that hydrocarbons of other than straight- or branched-chain structure were present.

Fraction γ_1, 33% of the total γ-compounds, was thus found to consist of: Saturated hydrocarbons, 40; unsaturated hydrocarbons, 40; and resins, 20%.

Examination of Fraction γ_2.—The residue after the γ_1-compounds had been removed was a brown powder. This on extraction with ethyl ether (which was complete within 3 or 4 days) and evaporation of the solvent, yielded a brick-red powder, m. p. 100—110°. Small quantities of acids and pyridine bases were removed and the powdered extract was then shaken with a dilute solution of sodium bisulphite with a view to remove aldehydes and ketones. Neither of these groups of compounds was present.

Continuing the examination according to Tschirch's scheme for the separation of resin acids, the washed material was saponified in benzene solution with 10% alcoholic potassium hydroxide. A portion, 15% of the total fraction, dissolved, forming a dark red solution from which a light brown, flocculent powder was precipitated on acidification with hydrochloric acid; it was a mixture of phenols and acids (Found: C, 75·5; H, 5·9; O, 18·4%). These were separated by bubbling carbon dioxide through a sodium hydroxide solution of the mixture. There were thus obtained four fractions: *Precipitated by carbon dioxide*, (1) a brown solid; (2) a red oil extracted by ether. *Not precipitated by carbon dioxide*, (3) an oily acid volatile in steam; (4) a solid, non-volatile acid.

Fraction (1) formed 80—85% of the total saponifiable material. It consisted of a mixture of complex phenols soluble in hot alcohol, from which they were obtained on evaporation of the solvent as a brick-red powder (Found: C, 75·6; H, 6·3; O, 18·1%). Neither the mixture of the phenols themselves nor that of their benzoyl derivatives (which were brown powders) had a sharp m. p. Fraction (2) was a red oil having a powerful odour of limonene.

Fraction (3) was present in small quantity only. It was a volatile unsaturated acid. Fraction (4), 15·20%, was a mixture of acids from which insoluble silver, iron, and barium salts were obtained. Benzoyl chloride, both in pyridine and in aqueous alkaline solution, effected benzoylation. The acids were therefore hydroxy-acids.

The saponifiable portion of the γ_2-fraction thus consisted of phenols and hydroxy-acids in the form of esters, similar to the resin

esters, or " resines " and " resinols," of Tschirch. The unsaponifiable portion was a dark red solid, m. p. 90—100°, free from nitrogen and sulphur (Found : C, 84·0; H, 7·2; O, 8·8%). In composition and general properties it closely resembled the resin separated from the γ_1-fraction. Tests showed that the oxygen it contained was not present in carboxylic, ketonic, aldehydic, or alcoholic grouping, but formed, presumably, a non-reactive bridged linkage. In its general inertness towards reagents, the substance was similar to the class of resins that Tschirch has termed " resenes."

Fraction γ_2, 37% of the total γ-compounds, was thus found to consist mainly of resins and resin-degradation products.

Examination of Fractions γ_3 and γ_4.—The residue from extraction with ethyl ether was a dark brown powder (m. p. 280—300° without decomp.). Acetone dissolved 40%, but the two fractions—γ_3, acetone-soluble, and γ_4, acetone-insoluble—were similar in composition (see Table II) and general properties. Both fractions were insoluble in alcoholic potassium hydroxide. Their resemblance to each other, and their dissimilarity from the γ_1 and γ_2 fractions, is best brought out by the results of destructive distillation and regulated oxidation, which will now be described.

Destructive Distillation of the Fractionated γ-Compounds.—One g. of each fraction was distilled in a small horizontal retort of Jena glass connected to an automatic Sprengel mercury pump. The retort was heated by an electric furnace, the temperature being raised slowly through intervals of 100° up to 450° and then of 50° to 600°. At each stage, the temperature was maintained constant until gases ceased to be evolved, a high vacuum being maintained, and the gases collected during each interval were analysed separately. The results are summarised in Table III.

TABLE III.

Destructive Distillation of Fractions of γ-Compounds.

A. Yields at 600°.

Fraction.	Total volatile matter, %.	Tar and oil, %.	Gas (c.c. per g.).
γ_1	(Distilled over unchanged below 300°.)		
γ_2	61·7	46·0	96·6
γ_3	48·3	13·0	140·5
γ_4	41·0	16·7	185·0

B. Gas analyses (%).

(Total gas over the range 15—600°.)

Fraction.	CO_2.	Higher olefines.	C_2H_4.	CO.	H_2.	Paraffins.
γ_2	5·2	2·0	1·0	6·5	32·5	54·4
γ_3	5·7	2·1	1·0	6·8	62·7	21·7
γ_4	6·2	2·3	1·7	9·5	52·0	28·2

The major portion of the tar from fraction γ_2 distilled between 200° and 300°. It consisted almost entirely of hydrocarbons. The residue was a dark brown, lustrous, intumescent mass, insoluble in chloroform. It will be seen that the gases evolved up to 600° contained a high proportion of paraffins.

The tars obtained from fractions γ_3 and γ_4 contained small quantities of phenols. The gases contained a high proportion of hydrogen and are thus dissimilar from the gases yielded by fraction γ_2. They more closely resemble the gases obtained from the β-fraction of the coal.

Oxidation of the Fractionated γ-Compounds.—Chemical analysis and the results of destructive distillation have thus shown the existence in the γ-compounds of three main types of constituents: hydrocarbons, resins, and a third group which has some of the characteristics both of resins and of coal-ulmins. The coal-ulmins, as exemplified by the β-compounds in particular, are readily oxidised, whereas the resins are not. We sought, therefore, to differentiate between the four γ-fractions by determining their relative ease of oxidation by hydrogen peroxide and dilute nitric acid.

Oxidation by hydrogen peroxide. One g. of each γ-fraction, as a fine powder, was treated under identical conditions with boiling hydrogen peroxide during 50 hours. The amount and character of the residues were then determined. The results are summarised in Table IV.

TABLE IV.

Oxidation of Fractionated γ-Compounds by Hydrogen Peroxide.

Fraction.	Residue, %.	Solubility of residue in KOH, %.	Analysis of residue.
γ_1	100	Nil.	
γ_2	90	Nil.	C, 78·1; H, 5·7; O, 16·2.
γ_3	Trace.	100	
γ_4	20	60	C, 70·8; H, 4·7; O, 24·5.

Fraction γ_1 was not affected by the treatment, but the more prolonged action of hydrogen peroxide removed the resinous material that this fraction contains, leaving hydrocarbons. Fraction γ_2 became lighter in colour and gradually lost its solubility in ether and in chloroform as it increased in oxygen content (compare Francis and Wheeler, J., 1925, **127**, 119). Fraction γ_3 reacted violently with each addition of hydrogen peroxide and was ultimately oxidised completely to water and oxides of carbon. Fraction γ_4 was not so reactive as γ_3, but was much more readily oxidised than γ_1 and γ_2. Much of the residue after oxidation was soluble in alkaline solutions, from which a brown, flocculent precipitate was obtained on acidification.

Oxidation by nitric acid. Since it was desired to avoid nitration, 30% nitric acid was used, 2·5 g. of the materials being boiled with 100 c.c. of the acid under reflux. Fraction γ_1 was not examined.

Fraction γ_2, which was rendered completely soluble in alkalis after 30 hours' treatment, showing that it contained no hydrocarbons, gave a copious evolution of nitrous fumes, and imparted a dark red colour to the nitric acid. The soluble acids (10%) did not contain picric acid. They were not further examined. The insoluble oxidation products (90%) were purified by washing with distilled water, dissolution in ammonia, and reprecipitation, as a reddish-brown powder, by dilute acid; further treatment with 30% nitric acid did not affect the composition (Found: C, 67·0; H, 4·6; O + N, 28·4%). The silver and copper salts of the acids were prepared and from combustion of the latter the equivalent was found to be 250.

Fractions γ_3 and γ_4 were treated together. The treatment, which was completed sooner than with fraction γ_2 and was accompanied by much frothing, rendered them completely soluble in alkalis. It was noted that the acids soluble in 30% nitric acid (10%) did not contain picric acid, but no further examination of them was made. The insoluble acids contained C, 60·9; H, 3·9; O + N, 35·2%, the composition remaining unchanged after further treatment with 30% nitric acid (Found: equiv., by combustion of copper salt, 268). As with similar products from fraction γ_2, benzene polycarboxylic acids were absent.

Whilst oxidation by hydrogen peroxide disclosed a difference in character between the γ_2- and the γ_3- and γ_4-fractions, oxidation by nitric acid shows a resemblance between all three fractions and a dissimilarity from coal-ulmins, such as the β-compounds from the same coal, which are rendered completely soluble in 30% nitric acid by prolonged treatment and yield both picric acid and benzene polycarboxylic acids (Francis and Wheeler, J., 1925, **127**, 2245).

We are in some doubt as to how the γ_3- and γ_4-fractions should be classed. The main bulk of any bituminous coal consists of groups of ulmin compounds, differing from each other according to the degree of condensation and dehydration they have experienced and differing, in consequence, as regards the extent to which they undergo colloidal dispersion in organic liquids. Just as the α-compounds are not dispersed in pyridine (whilst the β-compounds are), the β-compounds are not dispersed in chloroform; and it seemed possible that the γ_3- and γ_4-fractions might be ulmins that had been colloidally dispersed in chloroform.

In support of this suggestion, their low yield of tar and high yield of hydrogen on distillation in a vacuum, and their ease of oxidation by hydrogen peroxide, all relate them to the β-compounds. On the

other hand, they melt, without decomposition, at temperatures no higher than do many resin inclusions from bituminous coals. No ulmins that we have examined, whether synthetic or of natural occurrence, melt on heating—all decompose without fusing. Moreover, their presumed dispersion in chloroform (no ulmin compounds are soluble in chloroform) indicates that they have undergone less change during the coalification process than the β-compounds. They should therefore be more readily oxidised. They are not; and, moreover, their products of oxidation by nitric acid are such as are yielded by resins rather than by ulmins.

On the whole, we consider the γ_3- and γ_4-fractions to be more nearly akin to the resins, representing perhaps the degradation products of some intermediate stage in the production of resins in the plant metabolism, such as gives rise to, *e.g.*, the tannins.

We therefore specify the various fractions of the γ-compounds from a bituminous coal as follows:

γ_1 (soluble in light petroleum): Mainly hydrocarbons. In the example described, some 20% of resins were also present.

γ_2 (soluble in ethyl ether): Resinols, resines, and resenes.

γ_3 and γ_4 (insoluble in ethyl ether): Resin-like.

It may here be noted that the resins which occur macroscopically in bituminous coals are rarely of the same degree of solubility as modern resins, and the usual resin solvents, such as ether, alcohol, and benzene, do not dissolve them completely.

We have been surprised not to obtain direct evidence, in any of the coals that we have examined, of the presence of waxes (esters of fatty acids and alcohols). In the cuticles of modern plants, waxes invariably coat or permeate the cutin layer, whilst the cuticles that form so large a proportion of the Russian papierkohle have about 4% of wax associated with them (Legg and Wheeler, Safety in Mines Research Board Paper No. 17, 1925). Such waxes are particularly resistant to bacterial decay and one would expect them therefore to accumulate in the coal-forming deposits. The explanation of their absence is probably to be found in the behaviour of the montan wax of brown coals on being heated. Montan wax is a mixture of resins with carboceric and montan acids ($C_{27}H_{54}O_2$) both free and esterified with tetracosanol and ceryl and myricyl alcohols. The wax does not contain free hydrocarbons in any quantity, but it begins to decompose at about 200°, yielding solid and liquid hydrocarbons (Schneider and Tropsch, *Ges. Abh. Kennt. Kohle*, 1917, **11**, 28). It may be, therefore, that a portion of the free hydrocarbons found in bituminous coals (fraction γ_1) represents the waxes originally present.

As examples of the fractionation of the γ-compounds of other coals,

we may record the following (Table V). The coals are arranged in order of their carbon contents, the results obtained with Parkgate A being included for comparison.

TABLE V.

Fractionation of γ-Compounds.

(Percentages on ash-free, dry coal.)

	γ_1.	γ_2.	γ_3.
1. Vermilion County, Illinois, U.S.A. C, 76·7; H, 5·8.	2·13 (C, 86·0; H, 9·2.)	2·67 (C, 79·8; H, 6·3.)	1·20 (C, 80·3; H, 6·3.)
2.* Ayr Hard. C, 78·5; H, 5·9.	1·92	2·43	2·92
3.† Hamstead, Staffs. C, 79·3; H, 5·3.	1·06 (C, 85·9; H, 9·4.)	2·95 (C, 80·6; H, 6·5.)	0·98 (C, 79·7; H, 5·5.)
4.* Blackband. C, 79·5; H, 5·5.	2·37	2·85	2·28
5.* Top Hard. C, 80·1; H, 5·5.	1·61	2·40	2·62
6.† Wigan Six Feet. C, 82·0; H, 5·5.	2·92	1·57	3·67
7.† Parkgate B1, S. Yorks. C, 83·4; H, 5·5.	1·50 (C, 86·1; H, 9·3.)	1·75 (C, 84·0; H, 6·4.)	1·75
Parkgate B2, S. Yorks. C, 83·2; H, 5·8.	1·60 (C, 86·2; H, 9·2.)	4·20 (C, 84·0; H, 6·7.)	1·40 (C, 80·2; H, 5·9.)
8.† Ten Feet, Staffs. C, 83·4; H, 5·4.	2·30	2·16	4·34
9.† Parkgate A, S. Yorks. C, 83·6; H, 5·4.	2·30 (C, 83·9; H, 9·0.)	2·54 (C, 82·7; H, 6·9.)	2·06 (C, 79·5; H, 5·8.)
10.† Silkstone, S. Yorks. C, 83·6; H, 5·4.	2·26	1·52	5·14
11.† Arley, Lancs. C, 84·3; H, 5·4.	1·52	2·30	5·18
12.† Busty (Tudhoe), Durham. C, 85·1; H, 5·4.	1·72 (C, 88·4; H, 9·0.)	2·59 (C, 86·1; H, 6·5.)	3·68 (C, 84·4; H, 5·7.)
13.† Busty (Beamish Mary), Durham. C, 87·8; H, 5·4.	1·35	1·56	5·91

* Durain portion. † Clarain portion. The Hamstead clarain contained a high proportion of vitrain streaks.

The Parkgate samples B1 and B2 (No. 7 in Table V) are of particular interest. They were chosen from a section of the seam taken about 12 miles from Parkgate A, as representing the upper and lower clarain bands in that seam. This seam is a good example of a banded coal in which the several bands are of considerable thickness and can be mined separately. Since the several bands have

distinctive properties, this is often desirable. The seam is characterised throughout the S. Yorkshire coal-field by the existence of a broad (1—2 ft.) central durain band with equally broad clarain bands above and below it (see Evans, "The Correlation of the Parkgate Seam," *Trans. Inst. Min. Eng.*, 1926, **71**, 451). The lower clarain band in this section differs from the upper in containing many bright bands in which, under the microscope, resin rods can be distinguished amongst the woody structures. Their presence has markedly increased the proportion of fraction γ_2 extractable from the coal. It is perhaps necessary to point out that, in records of a study of the chemical constitution of a banded bituminous coal, the character of the band investigated should be specified.

It was at one time held that a certain proportion of γ-compounds in a coal was essential if a good commercial coke was to be made from it (Illingworth, *J. Soc. Chem. Ind.*, 1920, **39**, 133T). This is probably true, in general, but it has long been realised that a measure of the quality of the coke that could be obtained from a coal was not given by its content of γ-compounds. This is not surprising in view of the varying proportion in which the several fractions, each having different characteristics, are present in the γ-compounds of different coals, as shown in Table V. The determination of the effectiveness of the several γ-fractions in causing the agglutination of the remainder of the coal during the process of coking throws considerable light on their properties. Coking tests were made on blends of the coal residues, left after extraction, with each one in turn of the γ-fractions from the same coal, in the proportions in which they originally existed. The blends were made by dissolving the extracts in chloroform and immersing the residues in the solutions. After being allowed to soak during several hours, the solvent was removed by evaporation in a vacuum. Throughout the operations, care was taken to avoid oxidation of any of the ingredients of the blends, since oxidation of any one of them adversely affects the quality of the coke yielded (compare Parr and Hadley, *Univ. Illinois Bull.*, 76, 1914). The test employed was that commonly used when attempting to assess the coking-value of a coal, *viz.*, the standard crucible test for the determination of "volatile matter" ("Interim Report on Methods of Analysis of Coal, 1923," Fuel Research Board, Survey Paper No. 2, H.M. Stationery Office). As an example of the results, we may quote those obtained when the coal used for the tests was Parkgate A clarain, which gives a good quality coke in practice. The following observations were made:

A blend of the separated α-, β-, and γ-compounds, in the proportions in which they were obtained from the coal, gave a hard, well-sintered coke-button of nearly the same character as did a sample of

the original coal, showing that the α- and β-compounds had not suffered any material change during their separation.

A blend of the α- and β-compounds with only the γ_1-fraction gave in most of the tests a hard, well-sintered coke-button. A rather friable residue was occasionally obtained, which may be attributed to the fact that it is difficult to obtain satisfactory admixture of the extracted coal and this oily extract—there is a tendency for the extract to remain on the surface of the coal and to be volatilised during the coking test before it has been able to exert its agglutinating action. All such tests necessarily suffer from the fact that they do not reproduce exactly the original conditions of existence of the extracted material within the coal substance.

A blend of the α- and β-compounds with the γ_2-fraction gave a hard, well-sintered, and slightly swollen coke-button.

A blend of the α- and β-compounds with either the γ_3- or the γ_4-fraction gave a barely coherent residue, easily powdered between the fingers.

A discussion of the conditions necessary for the production of a good commercial coke would be out of place in this journal, but it may be said that, with regard to the composition of the coal, success does not rest solely on the use of a coal containing a sufficiency of some " coking principle." In so far as the presence of a " coking principle " is necessary, the conclusion can be drawn from this research that the agglutinating medium during coke-formation consists of the resins and hydrocarbons contained in the coal or is yielded by those resins and hydrocarbons during the early stages of heating in the coke-oven.

The Treatment of Bituminous Coals with Benzene.

Under atmospheric pressure, boiling benzene removes very little from most bituminous coals, but under higher pressures it apparently dissolves more. The most important researches in which this method of treating coal has been employed are those of Fischer, Broche, and Strauch (*Brennstoff-Chem.*, 1924, **5**, 299; 1925, **6**, 33), following preliminary experiments of Fischer and Gluud (*Ges. Abh. Kennt. Kohle*, 1916, **1**, 54), who found that at a pressure of 50 atms. (b. p. of benzene about 288°), a bituminous coal yielded, after several treatments, as much as 6·7% of extract.

Fischer, Broche, and Strauch have indicated an important relationship between the character of the substances extractable by benzene under pressure and that of the coal treated, which may throw light on the character of the coalification process. Briefly, they suggest that their work shows that with increasing geological age of the coals the ratio of free hydrocarbons to resins

increases, whilst the decomposition temperatures of the resins are raised.

We considered it important to institute a comparison between the substances obtained by resolving a coal with pyridine and chloroform and what may be termed "pressure-benzene" extracts such as those described by Fischer, Broche, and Strauch. We therefore carried out experiments on a number of bituminous coals in a similar manner. As a preliminary, we wished to know the effect, if any, of preheating a bituminous coal in an inert atmosphere at 250—280° on the amount of extractable matter it would subsequently yield to benzene or chloroform in the cold, Harger (*loc. cit.*) having stated that preheating at as low a temperature as 200° has the effect of greatly increasing the amount soluble in chloroform. We therefore sought this information from Mr. H. Berry, of the staff of the Fuel Research Board, who has been carrying out such experiments, and we have the permission of the Director of Fuel Research to quote some of his results (see Table VI).

TABLE VI.

The Effect of Preheating Bituminous Coal on its Solubility in Chloroform and Benzene. (H. BERRY.)

Extractable matter (% on ash-free, dry coal).

Coal.	Parkgate Brights.*		Parkgate Hards.†		Barnsley Brights.*		Barnsley Hards.†	
Solvent.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.
Without preheating.	1·45	0·37	1·39	0·50	0·73	0·31	1·15	0·59
After preheating at 200°	1·01	0·41	1·56	0·73	0·86	0·15	1·45	0·53
After preheating at 250°	2·75	0·54	2·72	0·71	1·20	0·30	2·37	0·34
After preheating at 350°	5·88	1·35	4·63	1·61	5·15	0·68	4·44	1·27

* *I.e.*, clarain and vitrain. † *I.e.*, durain.

It would thus seem that a change in a bituminous coal, which may be decomposition of some ingredient, is effected by heating at temperatures higher than 200°. In the work on the coking power of coal by Fischer, Broche, and Strauch (who were well aware of this effect of preheating), its incipient decomposition was of little moment, but we were anxious to remove the extractable matter unchanged, for comparison with the γ-compounds. Our first pressure-benzene extractions were therefore made at 200°.

The coals were ground to pass a 10- and remain on a 40-mesh sieve, and were dried in a vacuum. The extractions were carried out in an autoclave in an atmosphere of nitrogen, 4 or 5 successive treatments of each coal with pure benzene being made. After removal of the

benzene, the extracts were obtained as dark brown, viscous solids. The following results, obtained with Parkgate A clarain, can be regarded as typical.

Treatment of Parkgate A Clarain with Benzene.—(*a*) *At* 200°. The extract amounted to 5·96% of the coal. This was fractionated according to the scheme adopted for the γ-compounds, and yielded:

	% of coal.
Soluble in light petroleum.	2·22 (C, 85·0; H, 9·0.)
Soluble in ethyl ether.	2·02 (C, 84·0; H, 6·8.)
Insoluble in ethyl ether.	1·72 (C, 82·5; H, 5·95.)

In physical character and general chemical properties the substances were similar to the corresponding fractions of the γ-compounds.

These results should be compared with those recorded in Table II, from which it will be seen that the pressure-benzene extraction at 200° has removed all the hydrocarbons but has left a proportion of the resins and resin-like substances undissolved. These were removed from the coal residue in the autoclave by extracting it in a Soxhlet apparatus with pyridine and treating the extract with chloroform, 1·1% of soluble material being obtained. This was partly soluble in ethyl ether, the proportions, expressed as percentages on the original coal, being: ether-soluble, 0·66 (C, 82·0; H, 6·8%), and ether-insoluble, 0·44 (C, 80·0; H, 6·2%). The total amount extracted from the Parkgate A clarain by treatment with benzene at 200°, followed by resolution with pyridine and chloroform, was thus 7·06%, a figure which compares closely with the percentage of γ-compounds (6·9) obtained from this coal by direct resolution with pyridine and chloroform.

(*b*) *At* 285°. In order to compare our results more closely with those of Fischer, Broche, and Strauch, we now extracted a sample of the same coal with benzene at 285°, using 6 successive treatments in the autoclave. The extract amounted to 7·3% on the ash-free, dry coal. It was fractionated with light petroleum and ether and yielded (per cent. on the original coal): soluble in light petroleum, 2·55 (C, 85·4; H, 9·2); soluble in ether, 1·97 (C, 84·2; H, 7·3); insoluble in ether, 2·78 (C, 79·4; H, 5·8). Resolution of the residual coal from the autoclave with pyridine and chloroform yielded a small quantity of material (about 0·7% on the coal) completely soluble in ether.

The higher temperature of extraction thus appears to have caused decomposition of part of the resins, with the result that the proportions of hydrocarbons and resin-like material insoluble in ether have been increased. Some other part of the coal-substance also

seems to have been decomposed. A direct comparison of the different fractionations (Table VII) will make this clear.

TABLE VII.

	Resolution by pyridine and chloroform.	Pressure-benzene extraction.	
		at 200°.	at 285°.
Soluble in light petroleum (hydrocarbons).	2·30* (C, 83·9; H, 9·0.)	2·22 (C, 85·0; H, 9·0.)	2·55 (C, 85·4; H, 9·2.)
Soluble in ethyl ether (resins).	2·54 (C, 82·7; H, 6·9.)	2·02† (C, 84·0; H, 6·8.)	1·97† (C, 84·2; H, 7·3.)
Insoluble in ethyl ether (resin-like substances).	2·06 (C, 79·5; H, 5·8.)	1·72‡ (C, 82·5; H, 5·6.)	2·78 (C, 79·4; H, 5·8.)
Total.	6·90	5·96	7·30

* Contains 20% of resins, owing to prolonged Soxhlet extraction.

† On adding the ether-soluble fractions (0·66 and 0·7%, respectively) obtained on resolving the residue from the autoclave with pyridine and chloroform, these figures become 2·68 and 2·67%, respectively.

‡ On adding the ether-insoluble fraction (0·44%) obtained on resolving the residue from the autoclave with pyridine and chloroform, this figure becomes 2·16.

The method used by Fischer, Broche, and Strauch to fractionate their pressure-benzene extracts was to pour them into light petroleum, causing separation of insoluble solids, which they termed *Festbitumen*. On filtering these off and evaporating the light petroleum, viscous oils (*Ölbitumen*) were obtained. From our results it will be realised that this method effected a separation of the hydrocarbons from the resins and the resin-like compounds, probably a better separation than in our experiments, since our prolonged extraction with light petroleum in a Soxhlet apparatus dissolved some of the resins. Particular interest therefore attaches to their deduction that the former increase in amount, at the expense of the latter, with the geological age of the coal. The principal data on which this deduction is founded are recorded in Table VIII.

In conformity with the higher proportions of hydrocarbons removable from the older coals, their pressure-benzene extracts as a whole were more mobile, the most mobile being that obtained from a Ruhr anthracite (not included in Table VIII). The results certainly suggest a gradual increase in the proportion of hydrocarbons contained in the coal as the process of coalification proceeds, if it is considered that no thermal decomposition has occurred at the high temperature of extraction employed. We can make no statement on this point regarding the German coals, but we can affirm that with all the British coals we have tested appreciable decomposition takes place, hydrocarbons being produced at the expense of resins (see, *e.g.*, Table VII). Apart from this disadvantage, we cannot

TABLE VIII.

Treatment of Different Coals with Benzene at 285°.

(Fischer, Broche, and Strauch.)

	Percentages on ash-free, dry coal.		
Description of coal.	Total extract.	Hydrocarbons (Ölbitumen).	Resins and resin-like compounds (Festbitumen).
Dilsburg, Saar. C, 74·3; H, 5·3.	1·98 (C, 84·5; H, 7·9.)	1·04 (C, 89·3; H, 9·6.)	0·94 (C, 87·0; H, 6·5.)
Lohberg, Ruhr. C, 79·3; H, 5·6.	4·60 (C, 87·6; H, 7·0.)	2·48	2·12
Altenwald, Saar. C, 85·5; H, 6·7.	4·56 (C, 86·3; H, 6·7.)	2·55	2·01
Dudweiler, Saar. C, 86·5; H, 5·2.	7·76 (C, 87·9; H, 6·7.)	5·10	2·66
Prosper, Ruhr. C, 88·3; H, 5·2.	7·45 (C, 91·3; H, 6·9.)	(Not determined.)	
Osterfeld, Ruhr. C, 89·5; H, 5·8.	5·0 (C, 91·6; H, 6·9.)	3·40	1·60
Thyssen, Ruhr. C, 90·3; H, 5·4.	7·60 (C, 88·5; H, 6·7.)	5·10 (C, 92·2; H, 7·2.)	2·50 (C, 89·6; H, 6·1.)

regard pressure-benzene extraction as a satisfactory method of resolving British bituminous coals, for it does not appear to be equally effective with all. For example, the Hamstead clarain, which was found to contain 5·0% of γ-compounds on resolution with pyridine and chloroform, only yielded 1·6% of extractable matter to benzene at 200° and 4·5% at 285°. At the latter temperature, marked thermal decomposition took place.

Fischer, Broche, and Strauch's method of pressure-benzene extraction has been employed for several coals by Bone, Pearson, and Quarendon (*Proc. Roy. Soc.*, 1924, *A*, **105**, 608). Having poured the benzene extract into light petroleum, the last-named authors fractionated the *Ölbitumen* with benzene-free light petroleum and the *Festbitumen* with ethyl alcohol, thus obtaining four portions which they describe as follows : " (I) A yellowish-brown, non-nitrogenous portion soluble in light petroleum. (II) A nitrogenous reddish-brown solid, of low softening point, soluble in a mixture of 4 parts of light petroleum and 1 part of benzene. (III) A non-nitrogenous resinous portion. (IV) A group of nitrogenous bodies of ' humic ' type " (*loc. cit.*, p. 613).

The main reason for describing fraction IV as " humic " (a synonym for ulmic) appears to have been that it contained 1·1—1·5% of nitrogen. Be that as it may, this fraction should correspond with our γ_3- and γ_4-fractions, if ethyl alcohol were an effective solvent for coal-resins. In our experience, this seemed doubtful. We

therefore subjected pressure-benzene extracts of the Parkgate A clarain to fractionation according to a variant of Bone, Pearson, and Quarendon's scheme, with the following results :

Extraction with Benzene.—(*a*) *At* 200°. Total extract, 6·00. Soluble on pouring into light petroleum, 2·00; soluble in ethyl alcohol, 0·90; insoluble in ethyl alcohol, 3·10, all as % on the ash-free, dry coal. The alcohol-soluble fraction was similar in character to the ether-soluble fraction obtained from the pressure-benzene extract at 200° previously described, but was less in quantity (see Table VII). The fraction insoluble in ethyl alcohol was now extracted with ethyl ether, resins amounting to 1·4% of the coal dissolving.

(*b*) *At* 285°. Total extract, 7·29. Soluble on pouring into light petroleum, 2·30; soluble in ethyl alcohol, 1·00; insoluble in ethyl alcohol, 3·99, all as % on the ash-free, dry coal. On extracting the alcohol-insoluble material with ether, resins amounting to 1·22% of the coal dissolved.

These results are summarised in Table IX and should be compared with those given in Table VII.

TABLE IX.

Fractionation of Pressure-Benzene Extracts of Parkgate A Clarain.

(% of ash-free, dry coal).

	Extracted at 200°.		Extracted at 285°.	
Soluble in light petroleum.	2·00 (C, 86·2; H, 9·1.)		2·30 (C, 85·9; H, 9·4.)	
Soluble in ethyl alcohol.	0·90 (C, 83·2; H, 6·75.)	2·30	1·00 (C, 83·4; H, 6·8.)	2·22
Soluble in ethyl ether.	1·40 (C, 84·5; H, 6·9.)		1·22 (C, 84·5; H, 7·2.)	
Insoluble.	1·70 (C, 82·6; H, 6·0.)		2·77 (C, 80·1; H, 5·9.)	

The fraction of the Parkgate A clarain which would be described by Bone, Pearson, and Quarendon as " humic " (fraction IV) thus contained about 30—45% of resins; the remainder was what we have termed resin-like.

The research of Bone, Pearson, and Quarendon, like that of Fischer, Broche, and Strauch, deals with the probable importance of the various fractions of the pressure-benzene extracts as regards the coking power of the coals containing them. We propose to discuss this subject in detail in a communication to a technical journal, but may here note that Bone, Pearson, and Quarendon correlate the coking power of a coal with its content of that portion of the pressure-benzene extract (at about 285°) insoluble in light

petroleum and ethyl alcohol (their "Fraction IV"). We have shown that this fraction (in the coals that we have examined) consists of two classes of compounds—resins, soluble in ethyl ether, and compounds, allied to the resins, insoluble in that solvent. "Fraction IV," from the Parkgate A clarain, contains about 30% of ether-soluble and 70% of ether-insoluble compounds, but in this material from other bituminous coals the proportions are different. Apart from general considerations regarding the coking process, into which we need not here enter, it is therefore difficult to attach value to an apparent relationship between the coking power of a coal and its content of such indefinite constituents (or, in part, products of thermal decomposition).

The observations of Fischer, Broche, and Strauch on the change in character of the substances extractable from a coal with its geological age, or degree of coalification, seem to us to require, and to merit, amplification. We have therefore undertaken an examination of a series of coals, from the same seam, of increasing carbon content, adopting the method of resolution described in the first portion of this paper.

Much of the information contained in this paper was obtained during the course of an investigation that we are carrying out for the Safety in Mines Research Board, to whom we are indebted for permission to utilise it. Our thanks are also due to Mr. A. L. Godbert for a number of the data employed.

THE UNIVERSITY, SHEFFIELD. [*Received, October 15th*, 1926.]

CVI.—*The Constituents of the Cell-wall of the Flax Fibre.*

By ALBERT ERIC CASHMORE.

IN the past, investigations of the chemical constituents of the flax fibre dealt nearly always with materials, such as commercial raw fibre and yarn, in which non-fibrous tissues adhered to the fibre proper. This complex assemblage of tissues, comprising fragments of epidermis, cortex, soft-bast, and usually wood, contains a large variety of substances, and although it is customary to refer to the flax fibre as a pectocellulose, there is little definite knowledge of the distribution of the pectic constituents among the various tissues present in the raw fibre. Moreover, the loss in weight suffered by linen materials in the preliminary treatments with boiling alkalis is generally attributed, on very insecure grounds, to the removal of pectic constituents. This assumption is based

mainly on the evidence of Kolb (*Bull. Soc. Ind. Mulhouse*, June, 1868. See also Cross and Bevan's "Cellulose," 1918, p. 218), who states that pectic acid is precipitated when the spent alkaline lyes obtained in the kier-boiling of linen are acidified.

During the past few years our knowledge of the chemistry of pectin has been considerably enlarged (see, for example, Carre, *Ann. Bot.*, 1925, 811, where a summary of the literature dealing with the properties and constitution of pectin is given) and better methods have been devised for the extraction of pectin from plant tissues and for its estimation, either after extraction or *in situ*. Honneyman (*J. Text. Inst.*, 1925, **16**, 370T) has recently carried out estimations of pectin in commercial flax fibre, using the method of Ling, Nanji, and Paton (*J. Soc. Chem. Ind.*, 1925, **44**, 253T), and has shown that the pectic content of the retted fibre is very low (some 4—6%), whereas by the action of boiling dilute alkalis the fibre loses some 25% in weight. Similar results have been obtained in unpublished work carried out in these laboratories, and it has been shown that the fibres, freed from extraneous tissues by treatment with a hot soap solution as described later, contain less than 1% of pectin.

Reference may be made at this point to a paper by Schmidt, Haag, and Sperling (*Ber.*, 1925, **58**, 1394) on the so-called incrusting substances of flax. The authors do not state definitely the nature of the material used, but presumably it was the retted and scutched fibre of commerce. By successive treatments of the material with solutions of chlorine dioxide and sodium sulphite, a separation of the "incrusting" substances was effected, leaving the "skeletal" substances. In this way, the following figures were obtained:

Skeletal substances	49·9% (wt. of ash deducted).
Incrusting substances	38·9% (wt. of ash deducted).
Moisture content	7·7%.

The skeletal substances so obtained contained 3·8% of a hemicellulose soluble in cold 5% sodium hydroxide solution, and when this was removed the residual "cellulose" still contained 5% of "pentosan." The cellulose content of the fibre thus indicated is only about 40%, and it is clear that the "incrusting substances" of these authors include the bulk of the non-cellulosic constituents of the fibre wall with which we are concerned in this communication. There is, however, no evidence as to which of the constituents examined by them came from the fibre-strands and which from the adherent tissues.

In a paper entitled "The Incrustations of Flax," Ehrlich and Schmidt (*Biochem. Z.*, 1926, **169**, 13) describe the substances obtained by the extraction of flax straw with water at temperatures

varying from 50° to 130°, but in this case also no evidence was given to show from which tissues the substances examined were derived.

The fibre employed in the present investigation was obtained from unretted flax straw of good quality, pulled at about the customary stage of ripeness. This was broken and scutched without retting, and after hand-combing to remove the bulk of the adherent shives, was extracted with a hot soap solution. In this way, the remaining adherent tissues were loosened from the fibre-strands, and, as microscopic examination showed, could be completely removed by careful washing. The adherent tissues could not be readily removed from retted fibre by this treatment. It was found that the unretted fibre-strands cleaned by the soap treatment lost practically nothing in weight when placed for several days in a retting tank containing actively retting flax straw. It may be concluded, therefore, that the fibre-strands from unretted straw, purified as described, contained no appreciable amount of substances which are normally removed in retting. In order to remove small quantities of waxy and resinous constituents, the fibre-strands were next extracted with a mixture of ethyl alcohol and benzene. The small remaining quantity of pectin was then removed by the prolonged action of a hot dilute solution of ammonium oxalate. Finally, the fibre was leached with a cold 4% solution of sodium hydroxide, in order to remove free hemicelluloses.

The fibre-strands, after such purification, still contain some 15—16% of substances which may be removed by the action of boiling dilute alkalis, such as 2% sodium hydroxide or barium hydroxide solution. The nature of these alkali-soluble constituents and their mode of attachment to the cellulose form the main subjects of this communication. Since the soap-cleaned fibre-strands contain no adherent tissues, and also since the middle lamella between the fibre cells clearly represents only a very small proportion by weight of the material, it may be concluded that the bulk of the alkali-soluble substances is associated with the cellulose of the cell-wall. The association of cellulose and alkali-soluble substances in the fibre-strands, purified by the method described, will be referred to as the *cellulose-complex*.

This cellulose-complex was found by Cross and Bevan's method to contain 88·5% of " total cellulose " and 76·5% of " α-cellulose." Since the loss in weight produced by the action of boiling dilute sodium hydroxide solution on the cellulose-complex amounted to some 16%, it would appear that the " total cellulose " estimated by Cross and Bevan's method must include some of the alkali-soluble constituents of the fibre, and that the substances removed

by the 17·5% solution of sodium hydroxide (employed in the α-cellulose estimation) must include all the alkali-soluble constituents. For the estimation of the cellulose content of the cellulose-complex, the alternative method described on p. 724 is to be preferred; this method showed the α-cellulose content to be 82—83%.

The substances extracted from the cellulose-complex by means of boiling dilute alkali solution showed no reducing properties. This method of resolving the cellulose-complex was not considered very promising, because most monosaccharides and polysaccharides are unstable in the presence of dilute alkalis (compare Nef, *Annalen*, 1914, **403**, 204; Nef, Hedenburg, and Glattfeld, *J. Amer. Chem. Soc.*, 1917, **39**, 1618; Glattfeld and Hawke, *ibid.*, 1918, **40**, 973). Subsequent hydrolysis of the alkaline extract with 1% sulphuric acid at 130—140° gave a solution possessing strong reducing properties.

A more promising method of attack was that of hydrolysis with dilute sulphuric acid, and by this means it has been possible to identify the more important constituents of the cellulose-complex. An attempt to break down the complex by means of 5% sulphuric acid at 100° showed that it is very resistant to acid hydrolysis, for the syrup obtained from the neutralised hydrolysis liquors, when dried under diminished pressure, amounted to only 3% of the material taken.

By treatment with 1% sulphuric acid at 130—140° the breakdown was more complete. Thus, in one experiment, 100 g. of air-dried fibre yielded a syrup soluble in 90% alcohol, weighing 12·8 g. after drying. This syrup possessed a total reducing-sugar content of 61·7%, calculated as glucose. It was possible to identify glucose, galactose, xylose, and fucose among the products of hydrolysis. On analysis, the following results were obtained: free pentose (as xylose), 10·4; methylpentose (as fucose), 9·4; galactose, 14·8, 16·3; glucose, 29·7%. With more concentrated sulphuric acid (3 and 5%), the yield of syrup was greater, mainly owing to the more extensive production of glucose. The non-reducing constituents of the syrup obtained in the acid hydrolysis have not been identified. In part, they may arise by the further action of the acid on the sugars produced by hydrolysis, for Davis and Daish (*J. Agric. Sci.*, 1913, **5**, 437) have shown that the hydrolysis of maltose by means of 2—4% hydrochloric acid at 100° is accompanied by the decomposition of a considerable amount of the resulting hexoses.

The glucose produced by hydrolysis at 130—140° in all probability is not entirely due to the breakdown of the cellulose. This

is shown by the comparison, given on p. 727, of the results obtained before and after the cellulose-complex has been extracted with boiling alkali.

The resistance of the cellulose-complex to hydrolysis with 5% sulphuric acid at 100° suggests that the sugar groups are attached to the cellulose by a linkage of a glucosidic nature (compare Mehta, *Biochem. J.*, 1925, **19**, 958. Lignocellulose also is very resistant to hydrolysing agents and from this it is assumed to be a glucoside). The " -uronic anhydride " content of the cellulose complex (compare Ling, Nanji, and Paton, *loc. cit.*) is about 1·5%, amounting therefore to some 10% of the non-cellulosic constituents. Only traces of " -uronic anhydride " were found among the products of hydrolysis, but these groups are stated to be unstable to dilute acids at high temperatures (compare O'Dwyer, *Biochem. J.*, 1926, **20**, 657) and are completely decomposed by 12% hydrochloric acid at 100°.

Finally, the hydrolysis of the cellulose-complex by water has been investigated. At 100°, the action of the water was negligible, but at 140—150° a loss in weight of some 6% was produced, the hydrolysis being completed in less than 3 hours. The water-soluble products of hydrolysis consisted of (*a*) a hemicellulose, insoluble in 70% alcohol, amounting to some 4% of the weight of the fibre, (*b*) a resinous substance soluble in 70% alcohol, amounting to about 1% of the weight of the fibre.

The hemicellulose was finally obtained as a white, hygroscopic powder, containing some 21% of " -uronic anhydride " groups and possessing a neutral reaction. Careful hydrolysis with dilute sulphuric acid showed the presence of galactose and rhamnose groups, but no other sugars could be detected. Proximate analysis yielded the following results: galactose, 60; methylpentose (as rhamnose), 10·8—14·2; free pentose, 0—4; -uronic anhydride, 20·6; ash (mainly CaO), 4·8%.

The hemicellulose was not identical with the pectin extracted from flax-straw by Ehrlich (*loc. cit.*) by the action of water under pressure, as this substance contained more than 60% of " -uronic anhydride."

The soluble resinous substance was not obtained in a pure state, but on hydrolysis with dilute sulphuric acid it yielded about 25% of pentoses, and the residue was a resin of acid nature which has not been further investigated. The pentoses have been identified as fucose and xylose, present in equivalent amounts. The resinous substance contained neither galactose nor " -uronic anhydride " groups.

The fibre after extraction with water at 140—150° was still quite strong, and the cellulose was not apparently attacked. Extraction with water at higher temperatures was carried out, but

even at 170° the subsequent loss in weight amounted to only about 3—4%, although the fibre was weakened considerably. The aqueous extract has been examined, but no appreciable amount of non-cellulosic substances has been isolated. This is somewhat surprising in view of the fact that the fibre after extraction with water at 140—150° still contains some 10% of substances soluble in dilute sodium hydroxide solution at 100°, and also that the "-uronic anhydride" content of the fibre is still about 0·7%.

It would seem that the non-cellulosic portion of the flax fibre is made up, in part, of a hemicellulose bound to the cellulose either by a glucosidic linkage or by means of the carboxyl of the "-uronic anhydride" group. The residual non-cellulose material is evidently very firmly fixed to the cellulose, but its nature has not yet been characterised.

Experimental.

Preparation of the Clean Fibre.—The fibre was obtained from unretted straw (Somerset 1923 crop—good quality) by breaking, scutching, and combing. The last operation removed most of the residual woody tissues. The root and bough ends of the fibre were discarded and the residue was subjected to the action of a dilute (0·5%) soap solution at 80° for 60 minutes, washed in water, and again leached with soap solution at 80° for 90—120 minutes. Washing was carried out by means of successive steeps in hot water until the wash-water was colourless. The loss in weight produced by this soap treatment amounted to some 25—30%, varying according to the thoroughness of the preliminary mechanical treatment. The fibre, after being dried at room temperature, was extracted with ethyl alcohol–benzene for 6 hours, and then with a 0·5% solution of ammonium oxalate at 95° for 24 hours in order to remove the pectin (Norris and Schryver, *Biochem. J.*, 1925, **19**, 676). It was then washed, and kept for 24 hours, with occasional agitation, in a cold 4% solution of sodium hydroxide, in order to remove free hemicelluloses (Norris and Schryver, *Biochem. J.*, 1925, **19**, 676). Finally, it was thoroughly washed and allowed to dry at room temperature. A sample of the fibre was given a further extraction with ammonium oxalate at 95° for 24 hours, but the liquor was free from pectin.

Isolation of a Hemicellulose from the 4% Aqueous Sodium Hydroxide Extract.—The alkaline mother-liquor was filtered from the purified fibre-strands, and again through glass wool. The pale yellow liquor possessed no reducing properties; a small portion, acidified with acetic acid, was treated with calcium chloride, but no gel was precipitated. It was therefore assumed that pectic acid was not present in the solution.

The main portion was rendered distinctly acid with acetic acid and 1·5 volumes of 90% alcohol were added (compare O'Dwyer, *Biochem. J.*, 1923, **17**, 500), whereupon a pale brown gel was slowly precipitated. This was filtered off and redissolved in the minimum amount of hot water; the opalescent solution was allowed to cool, and the hemicellulose precipitated by addition of alcohol as before. These operations were repeated and the precipitate was kneaded successively with 70%, 90%, and 98% alcohol and finally with ether. It was then exposed to the air for a short time and finally dried in a vacuum over phosphorus pentoxide. The very pale brown powder thus obtained darkened slowly on exposure to the air, was soluble in hot water, and possessed no reducing properties. It gave the pentose reaction with phloroglucinol and hydrochloric acid, and Tollens's naphtharesorcinol reagent (*Ber.*, 1908, **41**, 1788) also gave a positive reaction, indicating the presence of " -uronic anhydride " residues.

An attempt to purify the hemicellulose by the method of Baker and Pope (J., 1900, **77**, 696) proved unsuccessful, as the blue copper complex dissolved when washed with the dilute alkali.

The yield of the purified hemicellulose was approximately 1% of the weight of the fibre [Found in different preparations : C, 41·8, 41·5; H, 6·5, 5·5 (on ash-free basis); ash, 3·4, 3·6; " -uronic anhydride," 22·8, 22·7, 22·85%].

Cellulose Content of the Fibre-Complex.—(*a*) Estimations by Cross and Bevan's method gave : Total cellulose, 88·5; α-cellulose, 76·5%. (*b*) The purified fibre lost 15—16% in weight by the action of 2% sodium hydroxide solution at 100° for 24 hours. After washing, it was immersed in a cold dilute solution of sodium hypochlorite (containing 0·7 g. of available Cl per litre) for 24 hours, and the residual non-cellulosic substances were removed by the action of 1% sodium carbonate solution at 100° for 2 hours. The loss in weight amounted to less than 2%. From these figures, it appears that the α-cellulose content of the dry purified fibre-strands amounted to 82—83%.

The " -uronic anhydride " content of the cellulose-complex amounted to about 1·8—2·0%; after extraction with 2% sodium hydroxide solution at 100° for 24 hours, the " -uronic anhydride " content, estimated by the method of Ling, Nanji, and Paton, had fallen to about 0·4%.

Extraction of the Cellulose-Complex with Dilute Alkali Solution at 100°.—A sample of the purified fibre-strands lost 15% in weight (allowing for moisture content) after extraction with 2% barium hydroxide solution at 100° for 5 hours.

The air-dried fibre (80 g.) was extracted at 100° for 5 hours with

700 c.c. of the barium hydroxide solution, and the mixture then filtered. The orange-coloured liquor did not reduce Fehling's solution; after neutralisation with sulphuric acid and filtration, the liquor was decolorised with norit and hydrolysed with 1% sulphuric acid at 130—140° for 3 hours. The liquor was then neutralised with barium carbonate, and the filtrate concentrated under diminished pressure to a brown syrup (10·6 g. after drying under diminished pressure over sulphuric acid), which possessed reducing properties. The total reducing-sugars (calculated as glucose) amounted to only 24·5% of the weight of the syrup. The syrup gave positive reactions for pentoses, but only small amounts of these were present. Galactose was isolated from the syrup by means of its α-methylphenylhydrazone (needles, m. p. 190°); a mixed melting point with an authentic specimen showed no depression. The galactose content of the syrup was estimated by oxidation to mucic acid by means of nitric acid (*d* 1·15) [A. W. van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren" (Borntraeger, Berlin), 1920, p. 123]: 2·13 g. of dry syrup gave 0·148 g. of mucic acid, m. p. 213° (*op. cit.*, p. 106); galactose, 9·8%. The syrup was not further examined.

Hydrolysis of the Cellulose-Complex with Dilute Sulphuric Acid.—(1) *At* 100° *with* 5% *sulphuric acid.* The air-dried fibre (50 g.) was immersed in 300 c.c. of 5% sulphuric acid, and the mixture was warmed for 2 hours on a boiling water-bath, maintained at 100° under reflux for 5 hours, cooled, and filtered. The residual mass was well washed with water, and the washings and filtrate were warmed on the water-bath and neutralised with powdered barium carbonate. The mixture was filtered, and the mother-liquor concentrated under diminished pressure to a brown syrup. This, together with the dry precipitate, was extracted three times with boiling 90% alcohol, and the extract filtered rapidly; the filtrate was warmed with norit and concentrated to a syrup, which was finally dried in a vacuum over sulphuric acid. The yield was 1·5 g. of a brown syrup which gave the pentose reaction with phloroglucinol and hydrochloric acid.

The pentose content of the purified fibre-strands, estimated by the Kruger–Tollens–Krober method (van der Haar, *op. cit.*, pp. 63—83), amounted to 3·4%; only 180 c.c. of distillate were collected in these pentose estimations, as recommended by Klingstedt (*Z. anal. Chem.*, 1925, **66**, 129).

(2) *At* 130—140° *with* 5% *sulphuric acid.* (a) The air-dried fibre (25 g.) was immersed in 300 c.c. of 5% sulphuric acid and heated in an autoclave for 2½ hours at a pressure of 30—40 lb.

per sq. inch. The mixture was then cooled, filtered, and subjected to the treatment outlined in the previous experiment. The yield of syrup soluble in 90% alcohol was 4·8 g. after drying to constant weight in a vacuum over sulphuric acid [Found : free pentose (as xylose), 6·1; methylpentose (as fucose), 6·2; galactose, 11·5; total reducing-sugars (as glucose), 47%].

Examination of the insoluble barium salts. These were extracted three times with boiling water and the filtrate was nearly neutralised with dilute sulphuric acid, filtered, and concentrated under diminished pressure, yielding a small amount of a syrup which gave a positive reaction for " -uronic anhydride " with Tollens's naphtharesorcinol reagent. Attempts were made to isolate the " -uronic acid " as the cinchonine salt, but without success.

(b) The air-dried fibre (100 g.) was hydrolysed with 600 c.c. of 5% sulphuric acid as before, and after the usual treatment the syrup soluble in 90% alcohol weighed 27 g. It was dark brown, and this colour was not completely removed by boiling the aqueous solution of the syrup with norit [Found : free pentose (as xylose), 10·4; methylpentose (as fucose), 6·8; galactose, 7·0%].

(3) *At* 130—140° *with* 1% *sulphuric acid.* The air-dried fibre (100 g.) was hydrolysed with 600 c.c. of 1% sulphuric acid as before, at a pressure of 30—40 lb. per sq. inch, for 3 hours. The yield of yellowish-brown syrup was 12·8 g. [Found : free pentose (as xylose), 10·4; methylpentose (as fucose), 9·7; galactose, 14·8, 16·3; glucose (by fermentation), 29·7; total reducing-sugars (as glucose), 61·7%]. The glucose was estimated by fermentation with yeast for 3 hours at 35° in a Lohnstein apparatus.

Identification of Monosaccharide Groups.—(a) *The hexose groups.* Glucose was identified as the *p*-nitrophenylosazone, m. p. 250°; galactose as the α-methylphenylhydrazone, m. p. 190°, and as the *o*-tolylhydrazone, m. p. 175°. The absence of fructose in the syrup was ascertained by the fact that Pinoff's reagent (van der Haar, *op. cit.*, p. 91) gave no colour when warmed with the syrup.

(b) *The pentose groups.* Many of the typical pentose reactions are obscured by the presence of hexoses in large amount; the pentoses were accordingly separated from the dry syrup (10 g.) by two extractions with boiling absolute alcohol (20 c.c.), the extract being filtered after cooling. Galactose and glucose are sparingly soluble in this solvent, whereas the pentoses are moderately easily soluble. The extract was concentrated to small bulk, and the product gave positive pentose reactions with Bial's reagent and Neumann's reagent; a spectroscopic examination of the latter colour indicated a strong band in the red, the absorption being weaker in the yellow part of the spectrum. This indicates the pres-

ence of xylose, and confirmation was obtained by means of Bertrand's reaction (*idem*, *ibid.*, p. 58), whereby the characteristic boat-shaped crystals of the cadmium bromide–cadmium xylonate ($CdBr{\cdot}C_5H_9O_6,H_2O$) were obtained after one crystallisation. Fucose was identified in the extract, by means of the α-methylphenylhydrazone (microcrystalline, rectangular plates, m. p. 181°) and the *as*-diphenylhydrazone (microscopic needles, m. p. 193—194°). The melting points given in the literature (*idem*, *ibid.*, p. 207) are 180° and 197—198°, respectively. As the m. p. of galactose α-methylphenylhydrazone has been recorded as 180° (compare von Ekenstein and de Bruyn, *Rec. trav. chim.*, 1896, **15**, 97, 225), the melting point of a mixture of galactose α-methylphenylhydrazone and the above α-methylphenylhydrazone was determined; the mixture melted indefinitely at 170—176°. Further confirmation was obtained by analysis of the α-methylphenylhydrazone (Found: C, 58·7; H, 7·1. Calc. for $C_{13}H_{20}O_4N_2$: C, 58·2; H, 7·4%).

The Presence of Glucose among the Products of Hydrolysis of the Non-cellulose Portion of the Complex.—The results summarised in Table I indicate that the glucose produced by the hydrolysis of the cellulose complex is derived in part from the non-cellulose constituents. In experiments (*a*), (*d*), and (*e*), the hydrolysis product was examined for galactose, but no trace of this sugar could be detected.

TABLE I.

Hydrolysis Experiments at 130—140°.

Material.	Hydrolysing agent.	% Glucose produced on dry wt. of material.	% Total reducing sugars (as glucose) on wt. of syrup.
(*a*) Purified fibre-strands after extraction with dilute sodium hydroxide solution at 100°	1% H_2SO_4	2·76	51·6
(*b*) Purified fibre-strands	1% H_2SO_4	4·30	61·7
(*c*) Purified fibre-strands	3% H_2SO_4	9·33	58·3
(*d*) Bleached linen	1% H_2SO_4	2·83	71·0
(*e*) Bleached linen	3% H_2SO_4	3·83	

Action of Water upon the Cellulose-Complex. Preliminary Experiments.—The fibre used in this investigation contained some 3·1% of total pentoses, 1·9% of methylpentose, 2·1% of "-uronic anhydride," and some 13·5% of substances soluble in 2% sodium hydroxide solution at 100°. The results in Table II were obtained on extraction with water at various temperatures.

The residual fibre after extraction at 140—150° for 3 hours contained 1·65% of total pentoses, 0·5% of methylpentoses, 0·7% of

TABLE II.

Temp. of extraction.	Time of extraction (hrs.).	% Loss in weight.
100°	6	0·3
115—120	6	1·0
140—150	3	6·5
140—150	6	5·8
140—150	12	6·3

" -uronic anhydride," and some 10·6% of substances soluble in 2% sodium hydroxide solution at 100°.

Action of Water at 140—150°. *Isolation of Hydrolysis Product Insoluble in* 70% *Alcohol.*—The fibre (about 200 g.) was extracted with water at 100° for 3 hours, washed with water, and then heated in an autoclave with 1200 c.c. of water for 3 hours at a pressure of 50—60 lb. per sq. inch. The aqueous liquors were collected, and concentrated to about 200 c.c. After treatment with norit and the addition of about 600 c.c. of 90% alcohol, a pale brown, flocculent substance was precipitated; this was separated by filtration, the filtrate being retained. The pale brown precipitate was redissolved in warm water, and the yellow solution treated with norit. This removed some of the colour, and after addition of alcohol the precipitate was nearly colourless. The process was repeated, the precipitate next leached successively with 90% alcohol, absolute alcohol, and ether, and finally dried in a vacuum over sulphuric acid. The colourless powder thus obtained was hygroscopic and easily soluble in water, giving a pale yellow solution. The yield of the pure substance amounted to some 3·5% on the weight of the fibre, but the crude substance was obtained in 5% yield. The aqueous solution gave no precipitate with dilute acids, alkalis, or salts such as calcium chloride or lead acetate, either in neutral or in dilute acetic acid solution. It did not reduce Fehling's solution on boiling. The Tollens naphtharesorcinol test gave evidence of the presence of " -uronic anhydride " groups and also a violet colour indicating the presence of rhamnose, which was confirmed by the Rosenthaler test (*Z. anal. Chem.*, 1909, **48**, 167; van der Haar, *op. cit.*, p. 48). Ketose groups were not present, as determined by Pinoff's test. The substance contained some 4·8% of ash which consisted mainly of calcium oxide. This ash was not easily removed, although the aqueous solution of the hemicellulose gave a crystalline precipitate with ammonium oxalate.

Analysis.—(1) The hemicellulose was dried in a vacuum over phosphorus pentoxide for each determination [Found: C, 42·5; H, 6·1 (on ash-free basis); ash, 4·7%].

(2) A sample was dissolved in water and a small amount of dilute acetic acid added; after two precipitations with alcohol, it

was dried as before [Found : C, 42·7, 42·8; H, 6·2, 5·9 (on ash-free basis); ash, 1·8, 1·8%].

" -Uronic anhydride " estimations. Found : " -Uronic anhydride," 20·8, 20·85, 20·3%.

Galactose estimations. The yield of mucic acid corresponded to 78% of galactose and galacturonic anhydride. Assuming that the " -uronic anhydride " group gave a 60% yield of mucic acid * the amount of galactose present in the hemicellulose would be about 60%.

Pentose estimations. In these estimations allowance was made for the " -uronic anhydride " group, which was assumed to give a 30% yield of phloroglucoside (van der Haar, *op. cit.*, p. 75) [Found : free pentose, 4·3, trace; methylpentose (as rhamnose), 10·5, 14·2%].

Hydrolysis of Hemicellulose.—Preliminary experiments were carried out on the action of dilute sulphuric acid at 100° upon the hemicellulose, the total reducing-sugars (calculated as glucose) being estimated by Pavy's method. The maximum yield of total reducing-sugars after 6 hours amounted to less than 60% and the liquor was brown, indicating decomposition of the products of hydrolysis. Hydrolysis for 3 hours with 1% sulphuric acid at 130—140° gave a yield of 83% of reducing sugars (as glucose).

Examination of the Products of Hydrolysis.—A solution of the hemicellulose (8·5 g.) in 250 c.c. of 2% sulphuric acid was heated for 7 hours on the boiling water-bath and at 130—140° for 1½ hours, and the liquor was neutralised with powdered barium carbonate and filtered. The filtrate, pale yellow after treatment with norit, gave a positive reaction for " -uronic anhydride " with Tollens's naphtharesorcinol reagent and reduced Fehling's solution in the cold. It was concentrated to a syrup under diminished pressure, and this syrup extracted twice with boiling absolute alcohol.

The alcoholic extract slowly deposited long, colourless crystals, m. p. 159°; a mixture of this substance with pure *d*-galactose melted at 159°. A small portion was converted into the α-methylphenylhydrazone (m. p. 190°).

The galactose was filtered from the alcoholic liquor, and the latter concentrated to a syrup under diminished pressure. This syrup gave positive tests for rhamnose with Tollens's naphtharesorcinol reagent and Rosenthaler's reagent. Neumann's orcinol test gave a pale yellow coloration, indicating the absence of free pentoses.

Rhamnose was identified as the *p*-nitrophenylosazone, a dark red precipitate which, after being dissolved in pyridine and repre-

* Ehrlich and Schubert (*Biochem. Z.*, 1926, **169**, 57) state that oxidation of *d*-galacturonic acid with bromine water gave a 60% yield of mucic acid.

cipitated with ether, melted at 234—235°. The phenylosazone also was prepared (m. p. 179—180°). Van der Haar (*op. cit.*, p. 227) gives m. p. 236° and 162°, respectively.

No other hexoses or pentoses could be detected among the products of hydrolysis. The nature of the "-uronic anhydride" group was not ascertained with precision, although it is evident, from the yield of mucic acid produced by the oxidation of the hemicellulose, that "galacturonic anhydride" is a component of this substance. The residue from the absolute-alcoholic extraction was dark brown and semi-solid. It was dissolved in water, and to the filtered solution 90% alcohol (4 vols.) was added, whereby a flocculent, pale yellow substance was precipitated. This was washed with absolute alcohol and ether and dried in a vacuum over sulphuric acid. The yield of the pale yellow powder was 0·5 g., the small yield being explained by the fact that *d*-galacturonic acid is unstable under the conditions of hydrolysis (see O'Dwyer, *Biochem. J.*, 1926, **20**, 657) [Found: Ba, 25·7. Calc. for $(C_6H_9O_7)_2Ba$: Ba, 26·2%]. An attempt to isolate crystalline *d*-galacturonic acid by Ehrlich's method (Ehrlich and Schubert, *loc. cit.*) was unsuccessful, a small amount of a syrup being produced, from which no crystalline cinchonine salt could be isolated. The syrup possessed strong reducing properties, even at the ordinary temperature.

Many modifications of the conditions of hydrolysis were made, but in no case was the yield of barium *d*-galacturonate greater than that produced above, and from the accumulated yield it was not possible to prepare crystalline *d*-galacturonic acid or its cinchonine salt. It is possible that a small amount of *d*-glycuronic acid may be present, which may inhibit crystallisation.

Action of Water at 140—150°. *Isolation of a Hydrolysis Product Soluble in* 70% *Alcohol.*—The brown 70% alcoholic mother-liquor, after removal of the insoluble hemicellulose described above, was concentrated to a syrup under diminished pressure, and the syrup dried to constant weight in a vacuum over sulphuric acid. The yield was approximately 1% of the weight of the fibre.

The syrup was dark brown, and gave a negative reaction for "-uronic anhydride." The presence of pentoses was indicated by Neumann's reagent, an olive-green coloration being obtained. Oxidation of a portion of the syrup with nitric acid (*d* 1·15) yielded no mucic acid, and therefore galactose was assumed to be absent [Found: free pentose (as xylose), 12·0; methylpentose (as fucose), 11·9%].

Hydrolysis of the syrup. The syrup was mixed with 100 c.c. of 1% sulphuric acid; it was not completely soluble, a small amount of dark brown substance remaining undissolved at the end of the

hydrolysis. The mixture was heated on the water-bath for 4 hours, norit added, and the mixture filtered. The filtrate was concentrated to a syrup under diminished pressure, and extracted (*a*) with boiling 98% alcohol, (*b*) with 80% alcohol. Fucose and xylose were identified in (*a*) by the methods previously described. No hexoses or pentoses were present in (*b*); the liquor on concentration gave a resinous substance, acid to litmus and insoluble in organic solvents other than aqueous alcohol, which was not further examined.

Action of Water at Higher Temperatures.—The fibre which had already been extracted with water at 130—140° was extracted with water at temperatures up to 170°. The aqueous extract, on concentration to small bulk, yielded only a small amount of a substance insoluble in 80% alcohol. By evaporation of the aqueous extract to dryness under diminished pressure, a small amount of a dark syrup was produced; this possessed slight reducing properties. The fibre lost some 3—4% in weight on extraction with water at 160—175° for 2 hours and was appreciably weakened. At temperatures above 175°, the fibre was disintegrated and the residue was very dark in colour.

It is proposed to examine the products obtained by the action of dilute alkali solution at 100° upon fibre which has been extracted with water at 135—140°. The fibre loses some 10% in weight by this treatment.

In conclusion, the author expresses his thanks to the Linen Industry Research Association for permission to publish the results of this investigation, and also to Dr. W. H. Gibson and Mr. C. R. Nodder for their kind interest and helpful suggestions.

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CVII.—*Constituents of* Myoporum Lætum, *Forst.* (The "Ngaio"). *Part II. Hydrogenation of Ngaione and Ngaiol and Dehydration of Ngaiol.*

By FREDERICK HENRY MCDOWALL.

THE presence of two double bonds in ngaione (J., 1925, 2200) has now been confirmed by the process of hydrogenation with Paal's colloidal palladium. Both ngaione and ngaiol, the secondary alcohol obtained from it by reduction, take up four atoms of hydrogen to form saturated *tetrahydro*-derivatives, $C_{15}H_{26}O_3$ and $C_{15}H_{28}O_3$. Tetrahydrongaione was characterised by the crystalline *picrolonate*

of *tetrahydrongaiylamine*, obtained from the ketone by reduction of its liquid oxime.

Attempts to obtain a dioxide from ngaione- and tetrahydrongaione-hydrazones by the methods of Woulff and Kishner have been unsuccessful.

The action of dehydrating agents on ngaiol has been exhaustively investigated. Concentrated formic acid at the boiling point gave a 50% yield of *ngaiol formate* [compare citronellol, which by this treatment gives citronellol formate almost quantitatively (Schimmel & Co., Report, 1901, 47), and caryophyllene, which with formic acid gives the formate of caryophyllene alcohol (Robertson, Kerr, and Henderson, J., 1925, **127**, 1944)]. On treatment with potassium hydrogen sulphate, ngaiol loses a molecule of water, to form *dehydrongaiene dioxide*,* $C_{15}H_{22}O_2$, but the yield is not large. *Ngaiylamine* was prepared from ngaioneoxime by reduction with sodium and alcohol, and converted into the phosphate. This, on dry distillation in a vacuum according to the method of Harries (*Annalen*, 1903, **328**, 91), yielded no product. Dilute aqueous (2*N*), 50% aqueous, and 10% alcoholic sulphuric acid caused racemisation and a slow change to a dehydrated compound, while complete resinification took place with 50% alcoholic sulphuric acid at 60—70° and with 80% aqueous sulphuric acid at 0°. This is in marked contrast to the behaviour of calameone, $C_{15}H_{26}O_2$, which easily loses two molecules of water when boiled for ½ hour with 10% aqueous sulphuric acid (Thoms and Beckström, *Ber.*, 1902, **35**, 3187). The best method of obtaining dehydrongaiene dioxide is by the action of alcoholic potash on the unstable *chloride*, formed by the action of thionyl chloride and pyridine on ngaiol.

Dehydrongaiene dioxide has a molecular refractivity corresponding to the presence of three double bonds, and with colloidal palladium takes up three molecules of hydrogen, yielding *tetrahydrongaiene dioxide*, $C_{15}H_{28}O_2$. The remarkable stability of two of the oxygen atoms in ngaiol to the action of dehydrating agents lends strong support to the conclusion that they are oxidic in character. They are not immune, however, from attack by oxidising agents, and it is hoped in a later publication to describe their behaviour on oxidation.

If Skita's colloidal palladium or platinum be used instead of Paal's palladium for the hydrogenation of ngaiol, the product contains a considerable proportion of a *glycol*, $C_{15}H_{30}O(OH)_2$, evidently formed through fission of one of the oxide rings by the hydrogenating agent. Since no trace of such a compound has been obtained

* The nomenclature is based on the hypothetical sesquiterpene, ngaiene, $C_{15}H_{24}$, corresponding to ngaione.

in the course of numerous experiments with Paal's colloid, it seems probable that the formation of the glycol is due to the slight acidity of Skita's reagent.

EXPERIMENTAL.

(a) *Hydrogenation.*—The hydrogen burette used was modelled on that of Francke (*Chem. Ztg.*, 1913, **37**, 958), the leading-tubes through rubber bungs being replaced by direct seals to a calibrated, thick-walled glass tube of about 5 cm. bore. The shaking-bottle was an ordinary 750 c.c. reagent bottle fitted with a hollow, ground-glass stopper joined to a tap and leading-tube, and held in by a clamp which gripped the top shoulder of the stopper.

The following modifications considerably decreased the tendency of the catalyst to become poisoned and lose its activity. During the preliminary evacuation, and also during the hydrogenation, alcohol vapour is drawn up and condenses in the rubber tubing; on the introduction of the hydrogen stream, this flows back into the hydrogenation bottle, carrying with it minute particles of rubber. A small inverted Kjeldahl trap was inserted on the leading-tube above the tap to prevent the reflux of any liquid that had been in contact with rubber, and a plug of cotton wool was inserted above the bulb to remove particles of rubber from the hydrogen stream. In default of a flexible copper connexion (Skita, *Ber.*, 1912, **45**, 4594), these precautions were found to ensure fairly regular results. Small particles of rubber were apt to be carried back from the side-tube of the receiver during the distillation at low pressure previous to hydrogenation. This defect was remedied by the use of a small Kjeldahl trap and a plug of glass wool in the side-tube of the external receiving tube.

Tetrahydrongaione. A suspension of ngaione (10 g., fractionally distilled at reduced pressure, and distilled again from a metal-bath immediately before use) in 100 c.c. of 50% ethyl alcohol was treated with a solution of Paal's colloidal palladium containing 0·05 g. of metal, and shaken with hydrogen at 1½ atm. pressure. The rate of absorption decreased steadily from the beginning, and several additions of fresh colloid were required during the course of the experiment. In the best circumstances, one molecular proportion was absorbed in 2½ hours, and further shaking for 10 hours completed the reaction. It was usually necessary, however, to extract and redistil the oil and to hydrogenate it with fresh colloid at least once before complete saturation could be reached. *Tetrahydrongaione* was obtained in 80% yield as a colourless, odourless oil, b. p. 196—198°/29 mm., $d_{20^\circ}^{20^\circ}$ 0·9977, $[\alpha]_D$ − 5·41°, $n_D^{20^\circ}$ 1·4652; $[R_L]_D$ 70·42 (calc. for $C_{15}H_{26}O_3$: $[R_L]_D$ 70·38) (Found: C, 70·6; H, 10·4.

$C_{15}H_{26}O_3$ requires C, 70·8; H, 10·3%). No trace of tetrahydrongaiol was observed in the product of hydrogenation.

The p-*nitrophenylhydrazone* and *oxime* were prepared as viscous liquids. The *semicarbazone* slowly crystallised to a waxy mass, but could not be recrystallised. Tetrahydrongaione oxime was therefore converted by reduction with sodium and alcohol into *tetrahydrongaiylamine*, a colourless, limpid oil with a strong odour, b. p. 198—200°/29 mm., $d_{20°}^{20°}$ 0·968, $n_D^{20°}$ 1·4718, $[R_L]_D$ 73·82 (calc. for $C_{15}H_{29}O_2N$: $[R_L]_D$ 73·78) (Found: C, 70·1; H, 11·6; N, 5·5. $C_{15}H_{29}O_2N$ requires C, 70·5; H, 11·5; N, 5·5%). *Tetrahydrongaiylamine picrolonate* was prepared in alcoholic solution and separated, after three crystallisations from alcohol, in bright yellow prisms, m. p. 184—185° (Found: N, 13·7. $C_{25}H_{37}O_7N_5$ requires N, 13·5%).

Dihydrongaiol. Ngaiol, purified through the acid phthalate (see Part I, *loc. cit.*), was treated as above described, the reaction being interrupted after the absorption of one molecule of hydrogen. Repeated distillation of the resulting oil yielded *dihydrongaiol*, a colourless, odourless oil, b. p. 199—202°/28 mm., $d_{20°}^{20°}$ 1·0009, $[\alpha]_D$ — 11·73°, $n_D^{20°}$ 1·4702, $[R_L]_D$ 70·86 (calc. for $C_{15}H_{26}O_3|^{=}_{1}$: $[R_L]_D$ 71·41) (Found: C, 70·9; H, 10·6; *M*, cryoscopic in benzene, 254. $C_{15}H_{26}O_3$ requires C, 70·8; H, 10·3%; *M*, 254). Acetylation yielded a *monoacetate*, a light yellow oil, b. p. 192°/29 mm., $d_{20°}^{20°}$ 1·0152, $n_D^{20°}$ 1·4631, $[R_L]_D$ 80·42, saponification value (by direct titration after saponification with absolute alcoholic potash), 186 ($C_{15}H_{25}O_2{\cdot}OAc|^{=}_{1}$ requires $[R_L]_D$ 80·78; S.V. 189).

Tetrahydrongaiol, the product of complete saturation of ngaiol with hydrogen under the above conditions, was obtained as a colourless, almost odourless, viscous oil, b. p. 202—206°/29 mm., $d_{20°}^{20°}$ 0·9917, $[\alpha]_D$ + 2·96°, $n_D^{20°}$ 1·4674, $[R_L]_D$ 71·76 (calc. for $C_{15}H_{28}O_3$: $[R_L]_D$ 71·88) (Found: C, 70·2; H, 11·0; *M*, cryoscopic in benzene, 264. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0%; *M*, 256). The product was free from glycol (see hydrogenation with Skita's reagent, later). Reduction of tetrahydrongaione with sodium and alcohol gave tetrahydrongaiol with physical constants almost identical with those recorded. The phenylurethane was obtained as a viscous syrup which did not crystallise even after removal of all adhering oil by distillation in steam.

Tetrahydrongaiol slowly decolorised aqueous potassium permanganate, but was quite unaffected by bromine in aqueous ether. Acetylation with acetic anhydride yielded *tetrahydrongaiol acetate*, a colourless oil with a slightly sharp odour, b. p. 205°/29 mm., $d_{20°}^{20°}$ 1·0096, $n_D^{20°}$ 1·4615, $[R_L]_D$ 81·06, saponification value, 184 (calc. for $C_{15}H_{27}O_2{\cdot}OAc$: $[R_L]_D$ 81·25; S.V. 187).

An attempt was made to prepare a di- or tri-acetate of tetrahydrongaiol by boiling this (2 g.) with freshly-distilled acetyl chloride (10 g.). The excess of acetyl chloride was then decomposed with sodium bicarbonate, and the oil was extracted with ether, and freed from solvent in a vacuum at 100° (Saponification value of the residual brown liquid, 200. Calc. for tetrahydrongaiol monoacetate, 194). The substance distilled at 1 mm. pressure without decomposition (unchanged refractive index) as a light yellow liquid, $n_D^{20°}$ 1·4682, $d_{20°}^{20°}$ 0·9973. A trace of chlorine was present (Found: C, 68·9; H, 10·3. $C_{15}H_{27}O_2 \cdot OAc$ requires C, 68·4; H, 10·2%). These results show that only a *monoacetate* had been formed, and that no dehydration had taken place (compare calameone, which by this treatment loses two molecules of water). The physical constants of the acetate obtained by this method indicate a considerable amount of isomerisation by the strongly acid reagent.

The glycol produced by hydrogenation of ngaiol. Ngaiol (10 g.) in 250 c.c. of 60% alcohol was shaken with colloidal platinum (prepared by inoculation of 10 c.c. of a 1% solution of chloroplatinic acid with colloidal palladium according to the method of Skita) at 2 atm. pressure. Two successive treatments yielded a colourless, viscous oil, which proved on fractionation to be a mixture of mono- and di-hydroxy-compounds.

Fraction I had b. p. 185—200°/21 mm., $d_{20°}^{20°}$ 0·9768, $n_D^{20°}$ 1·4664 (Found: C, 69·8; H, 11·4; *M*, by Rast's camphor method, 261. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0; *M*, 256. $C_{15}H_{30}O_3$ requires C, 69·7; H, 11·7%; *M*, 258). The acetate was prepared in the usual way with acetic anhydride, extracted with ether, and freed from ether in a vacuum at 100°. The light yellow oil thus obtained had saponification value 240. The fraction was therefore evidently a mixture of tetrahydrongaiol with an oxido-glycol.

Fraction III consisted of a fairly pure *oxido-glycol*, b. p. 217—220°/21 mm., $d_{20°}^{20°}$ 0·9734, $n_D^{20°}$ 1·4668, $[R_L]_D$ 73·58 {calc. for $C_{15}H_{28}O(OH)_2$: $[R_L]_D$ 73·96} (Found: C, 69·7; H, 11·8; *M*, by Rast's camphor method, 250. $C_{15}H_{30}O_3$ requires C, 69·7; H, 11·7%; *M*, 258). The acetate, prepared as described above, was an almost colourless oil, $n_D^{20°}$ 1·4550, saponification value 304 [$C_{15}H_{28}O(OAc)_2$ requires S.V. 326].

(b) *Action of Halogens and Halogen Acids.*—Ngaione and ngaiol are very sensitive to the action of halogens and halogen acids. When treated with iodine monochloride according to the Wijs method, ngaione gave the iodine value 101, and ngaiol the value 104, corresponding very closely to the theoretical values, 102 and 104, respectively, for the presence of one double bond. This failure of the Wijs method to give a correct indication of the extent of un-

saturation is not unusual with constituents of essential oils, but it is of interest that in each of the above cases one double linking is so definitely indicated.

Bromine water was only slowly decolorised, whereas bromine in cooled chloroform was rapidly absorbed by ngaione, giving a black tar, with evolution of much hydrogen bromide. Bromine in hydroxylic solvents, such as ether–alcohol (1 : 1) at — 10°, and glacial acetic acid, was rapidly decolorised by ngaione, and hydrogen bromide was then copiously evolved, even before the addition of one molecule of bromine was completed. The instability of the bromine addition compounds, especially in wet solvents, would account for the slow rate of decoloration of bromine water by ngaione and ngaiol. A crystalline bromide, or even a liquid compound with the bromine content of a dibromide, was not obtained in any of the above experiments.

When gaseous hydrogen bromide or hydrogen iodide was passed into their cooled glacial acetic acid solutions, ngaione and ngaiol were rapidly and completely resinified. The action of halogen acids on tetrahydrongaione and tetrahydrongaiol will be described in a later paper.

(c) *Hydrazones of Tetrahydrongaione and Ngaione.*—It has been shown by Woulff (*Annalen*, 1912, **394**, 86) and by Kishner (*Chem. Zentr.*, 1912, I, 1713; 1913, I, 706; *et al.*) that the carbonyl group of many ketones can be replaced by a methylene group by decomposition of their hydrazones (see also Staudinger, *Ber.*, 1911, **44**, 2197).

Tetrahydrongaione easily formed a hydrazone when heated in alcoholic solution for 6 hours with an excess of 90% hydrazine. Removal of the extracting ether in a vacuum at 100° yielded a thick, colourless oil, $n_D^{20°}$ 1·4920. This decomposed to a considerable extent on distillation, with much evolution of gas, the residue being presumably a ketazine. The distillate had b. p. 210—220°/13 mm. and $n_D^{20°}$ 1·4921 (Found: N, 9·9. $C_{15}H_{26}O_2{:}N{\cdot}NH_2$ requires N, 10·4%). The low value for nitrogen was probably due to the presence of a trace of ketazine. In subsequent experiments, no attempt was made to purify the hydrazone.

When tetrahydrongaionehydrazone was heated at 120—180° with a small lump of fused caustic potash or with platinised tile (Kishner, *loc. cit.*), some evolution of nitrogen took place; no oil was obtained volatile in steam, and it was evident that the reaction had stopped at the formation of the ketazine, a very viscous oil which did not crystallise after 6 months' standing.

Tetrahydrongaionehydrazone was decomposed by alcoholic sodium ethoxide in a sealed tube at 160—165°, and at 190—200°, giving an

inflammable gas, ammonia, and substances of approximate composition $C_{12}H_{22}O$ or $C_{14}H_{26}O$. Ngaionehydrazone under the same conditions formed a complex mixture of decomposition products, b. p. 120—210°/29 mm. The low-boiling portion had an odour resembling that of citral, whilst a fraction, b. p. 170—190°/29 mm., gave analytical values (C, 79·1; H, 11·2%) of no obvious meaning.

It is clear that the hydrazones are decomposed by sodium ethoxide with loss of carbon from the molecule, possibly owing to the presence of an oxide linking next to the carbonyl group. That this change is not wholly related to the oxide rings, but is an intrinsic property of the hydrazone, was shown by the fact that ngaiol remained completely unaltered, even as regards its specific rotation, when heated for 12 hours with alcoholic sodium ethoxide in a sealed tube at 160—170°.

The results suffice to show that it is not possible to obtain by this method the dioxides $C_{15}H_{24}O_2$ and $C_{15}H_{28}O_2$ from ngaione and tetrahydrongaione, respectively. The investigation of the reaction has therefore been left in abeyance until more is known of the structure of ngaione.

(d) *Action of Dehydrating Agents on Ngaiol.*—(1) *Concentrated formic acid.* Ngaiol (20 g.) was heated on the water-bath with 90% formic acid (70 g.) for 5 minutes. The acid was then neutralised with sodium carbonate, and the oil extracted with ether. Distillation gave 11 g. of a light yellow oil, b. p. 186—188°/26 mm., $d_{20°}$ 1·0387, $n_D^{20°}$ 1·4751 (Found: C, 69·5; H, 9·0; saponification value, 162. $C_{15}H_{23}O_2{\cdot}O{\cdot}COH$ requires C, 68·5; H, 8·7%; S.V., 200. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6%). The oil was thus a mixture of ngaiol and its formate, from which ngaiol was recovered with unchanged physical constants by saponification with alcoholic potash. Heating of ngaiol for ½ hour with 100% formic acid caused almost complete resinification.

(2) *Potassium hydrogen sulphate.* An intimate mixture of ngaiol (1 part) and the finely-powdered dehydrating agent (2 parts) was rapidly heated to 190° in an atmosphere of carbon dioxide. After ½ hour, the product was cooled, and distilled in steam. Extraction of the distillate with petrol gave a 40% yield of a mixture of about equal parts of ngaiol and *dehydrongaiene dioxide*, $C_{15}H_{22}O_2$. The latter was separated by fractional distillation as an orange-coloured oil with a somewhat tarry odour, b. p. 168—174°/29 mm., $d_{20°}$ 0·9689, $n_D^{20°}$ 1·4914, $[R_L]_D$ 70·03 (calc. for $C_{15}H_{22}O_2|\overline{=}_3$: $[R_L]_D$ 68·95). The high value of the molecular refraction may be due to the presence of conjugated double bonds (Found, for two different specimens: C, 76·2, 76·4; H, 9·6, 9·3. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). The substance rapidly absorbed oxygen from the air, forming a thick brown oil.

(3) *Treatment with zinc dust.* It has been shown by Semmler (*Ber.*, 1894, **27**, 2520; 1900, **33**, 776) and others (Gaudurin, *Ber.*, 1908, **41**, 4361; Ruzicka and Stoll, *Helv. Chim. Acta*, 1924, **7**, 100) that many alcohols are reducible by means of zinc dust at a high temperature. Ngaiol, however, was completely unaffected when heated with three times its weight of zinc dust at 210—220° in a sealed tube in an atmosphere of carbon dioxide, and even when heated at 250—260° for 4 hours it suffered no change other than slight decreases in the density and the optical rotation. No pressure was developed in the tube in either case.

(4) *Dry distillation of the amine phosphate.* Ngaione oxime was unaffected by sodium amalgam and acetic acid (compare Goldschmidt, *Ber.*, 1887, **20**, 486), but was easily reduced by sodium and alcohol, giving a 70% yield of *ngaiylamine*, a colourless, limpid, strongly odorous liquid which gradually turned brown in the air, b. p. 184—186°/29 mm., $d_{20^\circ}^{20^\circ}$ 0·9940, $[\alpha]_D$ − 18·63°, $n_D^{20^\circ}$ 1·4822, $[R_L]_D$ 72·07 (calc. for $C_{15}H_{23}O_2{\cdot}NH_2|^{=}_{2}$: $[R_L]_D$ 72·64) (Found: C, 71·4; H, 10·2; N, 5·6. $C_{15}H_{25}O_2N$ requires C, 71·6; H, 10·0; N, 5·6%). The amine was unstable to hot hydrochloric acid, but the double compound with platinic chloride could be prepared in the cold as a bright yellow solid, decomp. 170—180° [Found: Pt, 21·4. $(C_{15}H_{23}O_2{\cdot}NH_2)_2,PtCl_4$ requires Pt, 21·4%].

Ngaiylamine hydrobromide was obtained pure, by several crystallisations from a cold concentrated solution in absolute alcohol by addition of dry ether, in long, white, rectangular prisms, m. p. 190—191° (Found: Br, 24·1. $C_{15}H_{25}O_2N,HBr$ requires Br, 24·1%). Unlike the hydrochloride, it is not hygroscopic.

Benzenesulphonngaiylamide was prepared by the Schotten-Baumann process, and the resulting oil extracted with ether. The substance crystallised in elongated, rectangular prisms, m. p. 107—108° [Found: N (micro-Kjeldahl), 3·5. $C_{21}H_{29}O_4NS$ requires N, 3·6%].

Ngaiylamine picrolonate was obtained as a yellow powder, which formed amber-coloured prisms in radiating tufts on recrystallisation from warm absolute alcohol; m. p. 162—163°, independent of the rate of heating (Found: N, 14·0. $C_{25}H_{33}O_7N_5$ requires N, 13·6%).

(5) *Treatment with sulphuric acid.* Ngaiol (6 g.) was boiled with 2*N*-sulphuric acid (40 g.) for 1 hour, and recovered, by distillation in steam, without appreciable change in physical constants other than a 50% lowering of the specific rotation. Boiling with 33% sulphuric acid for 6 hours produced a resin, and also a substance, b. p. 182—189°/29 mm., $d_{20^\circ}^{20^\circ}$ 1·0008, $n_D^{20^\circ}$ 1·4802 (Found: C, 73·8; H, 9·5. Ngaiol, $C_{15}H_{24}O_3$, requires C, 71·4; H, 9·6%). A certain amount of

dehydration had thus taken place, but the product was impure, and the yield was small.

(6) *Dehydrongaiene dioxide prepared through ngaiyl chloride.* For the preparation of ngaiyl chloride, the Darzens process (*Compt. rend.*, 1911, **152**, 1314; Forster and Cardwell, J., 1913, **103**, 1341) was chosen as the most suitable in view of the sensitiveness of the ngaiol molecule to halogen acid (see p. 735). To a mixture of ngaiol (10·6 g.) and pure dry pyridine (3·6 g.; 1 mol.), thionyl chloride (5·4 g.; 1 mol.) was added slowly with shaking and cooling in ice. After standing for 1 hour at room temperature, the yellow product was decomposed by heating it on the water-bath for 1 hour, and the resulting oil was acidified and extracted with ether. On removal of the solvent a heavy, black, oily *chloride* was obtained which was very unstable, partly decomposing even at water-bath temperature. Distillation at 16 mm. pressure caused much decomposition with evolution of hydrogen chloride, and the distillate contained only 3% of chlorine (calc. for $C_{15}H_{23}O_2Cl$: Cl, 13·1%). The oil was therefore heated for 2 hours with *N*-alcoholic potash, and the product distilled in steam. The main portion of the resulting liquid, a yellow oil with a tarry odour, boiled at 170—175°/28 mm., $d_{20°}^{20°}$ 0·9751, $[\alpha]_D$ — 10·84°, $n_D^{20°}$ 1·4854, $[R_L]_D$ 68·90 (calc. for $C_{15}H_{22}O_2|\overline{=}_3$: $[R_L]_D$ 68·95) (Found: C, 76·7; H, 9·5. Calc. for $C_{15}H_{22}O_2$: C, 76·9; H, 9·5%). The yield was 45% of the theoretical. (Dehydrongaiene dioxide must be prepared and kept in an atmosphere of carbon dioxide, or other indifferent gas, since it easily absorbs oxygen from the air.)

iso*Dehydrongaiene Dioxide.*—Ngaiol can also be converted into a dehydrongaiene dioxide by the use of an excess of pure dry quinoline, instead of the calculated quantity of pyridine. The formation of an *iso*-compound under these conditions may be due to the fact that the solution never becomes acid—during the decomposition on the water-bath of the complex thionyl compound described above, the resulting ngaiyl chloride is partly decomposed with evolution of hydrogen chloride.

Quinoline (20 g.; 5 mols.) was mixed with ngaiol (9·3 g.; 1 mol.) at — 15° in a flask through which a stream of dry carbon dioxide was passing, and thionyl chloride (3·1 g.; 1 mol.) was slowly added. After 1 hour, the yellow product was decomposed by heating it on the water-bath for 1 hour, and the chloride present was then further decomposed by the excess of quinoline by heating the mixture at 150—160° for 1 hour. The product was poured into dilute acetic acid and distilled in steam in a current of carbon dioxide. From the resulting oil, which still contained a small quantity of chlorine, a fraction (1 g.) was isolated, free from chlorine, b. p. 168—174°/

29 mm., $n_D^{20°}$ 1·4801, $d_{20°}^{20°}$ 0·9654, $[R_L]_D$ 68·95 (calc. for $C_{15}H_{22}O_2|\overline{=}_3$: $[R_L]_D$ 68·95) (Found: C, 76·8; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). The physical constants indicate that the substance is an isomeride of the dehydrongaiene dioxide obtained by the use of pyridine, probably differing from it in the position of the double bond. The higher-boiling fraction consisted for the most part of unchanged ngaiol.

Tetrahydrongaiene Dioxide.—Dehydrongaiene dioxide (5·9 g.) (obtained by the pyridine method), in presence of Paal's colloidal palladium (7 c.c. of 1% solution) and 50% ethyl alcohol (100 c.c.), absorbed hydrogen only slowly, and several treatments were necessary before saturation was reached. Eventually a colourless oil was obtained, with a slight pineapple odour, b. p. 170—180°/29 mm., $d_{20°}^{20°}$ 0·9379, $n_D^{20°}$ 1·4631, $[R_L]_D$ 70·63 (calc. for $C_{15}H_{28}O_2$: $[R_L]_D$ 70·35) (Found: C, 74·9; H, 11·7. $C_{15}H_{28}O_2$ requires C, 74·9; H, 11·7%).

The author desires to thank Professor Inglis, of Otago University, New Zealand, for kindly arranging the supply of further quantities of ngaio oil. He is also indebted to the Department of Scientific and Industrial Research for a maintenance grant, and to the Chemical Society and the New Zealand Institute for grants towards the expenses of the research.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February 5th*, 1927.]

CVIII.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part XIII.*

By HUGH GRAHAM, ALEXANDER KILLEN MACBETH, and WILFRED BEAUMONT ORR.

IN the previous communication (J., 1926, 1248), it was shown that the dihalogen derivatives of a series of barbituric acids are reduced by hydrazine hydrate to the corresponding monohalogen compounds, and spectroscopic evidence was submitted which indicated that barbituric acid and its monohalogen derivatives exist in the enolic modification, whereas the dihalogen derivatives possess a definitely ketonic structure. Further support for this view has now been found in the absorption spectra of 1-phenylbarbituric acid and 1 : 3-diphenylbarbituric acid and their derivatives, the graphs for which are shown in Figs. 1—4. The parent acids and the monohalogen derivatives give absorption spectra showing well-defined bands characteristic of the enolic modification; the dihalogen compounds, on the other hand, show general absorption only.

Comparison of the various graphs shows that the spectra of the phenylbarbituric acids are of a much simpler character than the absorption spectrum of barbituric acid itself, the complex bands in the latter being replaced by a principal band extending over $1/\lambda$ 3700—4200. That this band is characteristic of the enolic modification is evident from the fact that it occurs in the presence of alkali,

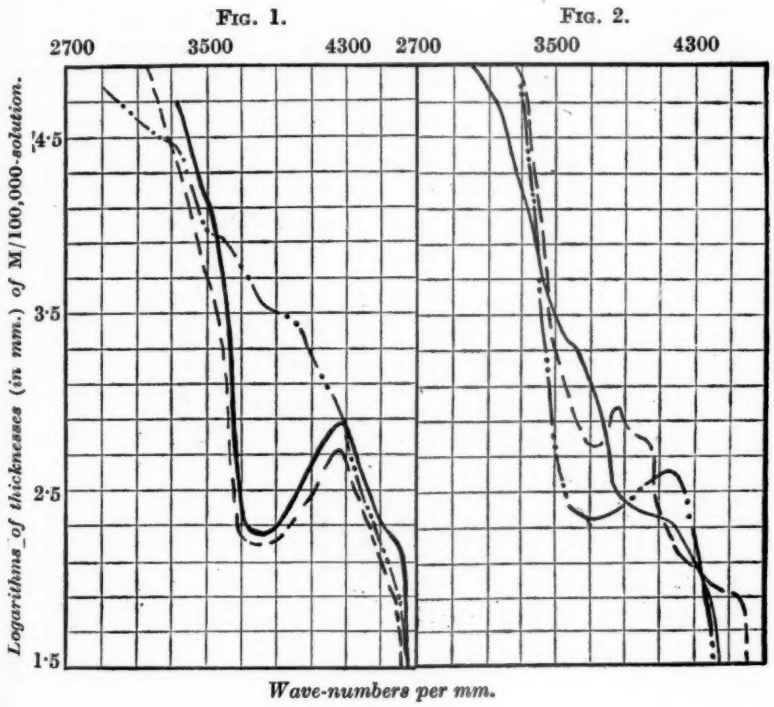


Fig. 1.

——————— 1-*Phenylbarbituric acid* (*in water*).
— — — — ,, + NaOH.
—·· —·· — ,, + HCl.

Fig. 2.

——————— 5 : 5-*Dibromo*-1-*phenylbarbituric acid* (*in alcohol*).
— — — — ,, + NaOEt.
— ·· — ·· — 5-*Bromo*-1-*phenylbarbituric acid* (*in water*).

and virtually disappears in the presence of hydrochloric acid; and since the band is only slightly more persistent in an alkaline solution than in an aqueous solution of the parent acids or their monohalogen derivatives, the latter also must exist in the enolic form.

The spectra of the dihalogen compounds (Figs. 2 and 4) undergo a marked change on the addition of alkali, the band characteristic

of the enolic modification developing to some extent. The decomposition of the dihalogen compound to the corresponding monohalogen derivative in alkaline solution is thus indicated, and additional proof of such change is given below.

For the purpose of comparison, the work was extended to the examination of absorption spectra of typical thiobarbituric acids,

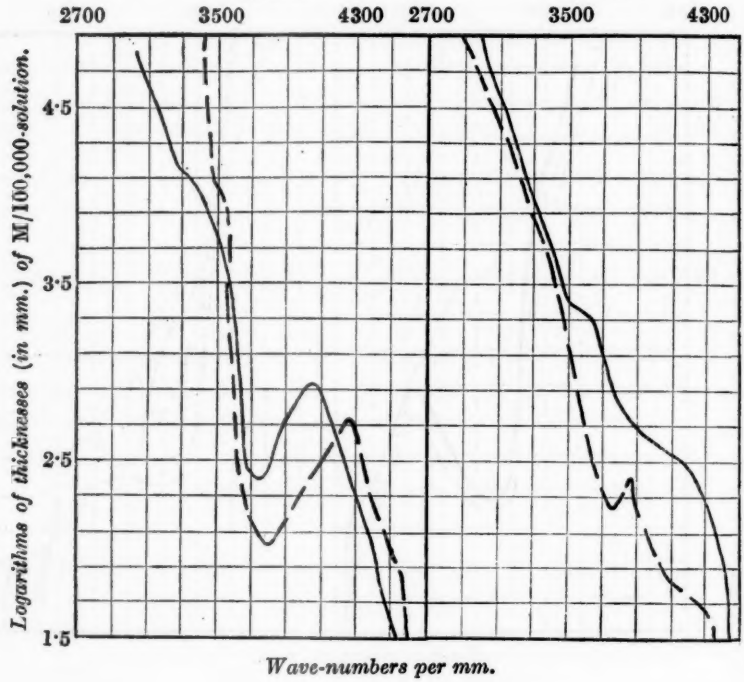


Fig. 3.

———— 1 : 3-*Diphenylbarbituric acid* (*in alcohol*).
— — — — „ + NaOEt.

Fig. 4.

———— 5 : 5-*Dibromo*-1 : 3-*diphenylbarbituric acid* (*in alcohol*).
— — — — „ + NaOEt.

and the results obtained with 2-thiobarbituric acid and 2-thio-1 : 3-diphenylbarbituric acid are shown in Figs. 5 and 6. The spectrum of the former presents a series of bands similar to those given by barbituric acid, whereas the diphenyl thio-analogue shows the simplification of absorption due, as already recorded, to the introduction of phenyl radicals. In the spectra of the thio-acids, however, the bands are all moved towards the visible region, as the

following values show. In 2-thio-1 : 3-diphenylbarbituric acid, the band of frequency 1/λ 3460 approximately corresponds with the band 1/λ 3760 of 1 : 3-diphenylbarbituric acid, and the bands of 2-thiobarbituric acid with approximate frequencies 1/λ 2980,

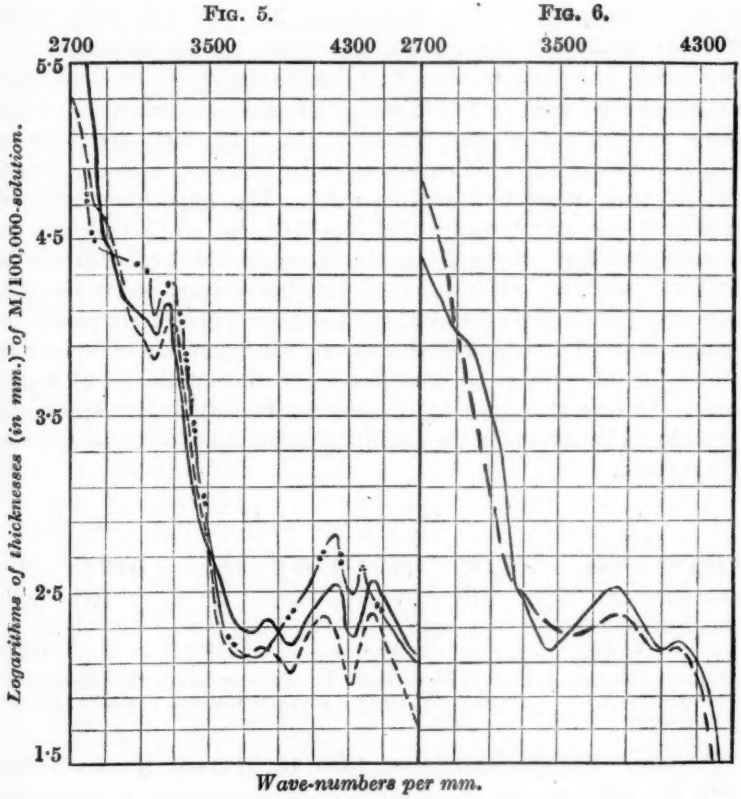


Fig. 5.

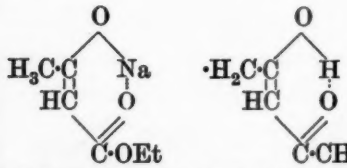
———— 2-*Thiobarbituric acid* (*in water*).
— — — — ,, + NaOH.
—·—·— ,, + HCl.

Fig. 6.

———— 2-*Thio*-1 : 3-*diphenylbarbituric acid* (*in alcohol*).
— — — — ,, + NaOEt.

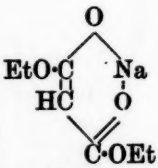
3550, 3760, 4120 correspond with those at 1/λ 3180, 3750, 3900, 4500 approximately in the absorption spectrum of barbituric acid. It would further appear that the enolic modifications of the thio-acids are very stable, as but little change takes place in the character of the absorption in the presence of acid.

Hartley (J., 1905, **87**, 1796) reported that barbituric acid transmitted a continuous spectrum through thicknesses of $M/1000$-solution up to 20 mm. This statement is surprising, as it has been found (Brannigan, Macbeth, and Stewart, J., 1913, **103**, 406) that the sodium derivatives of malonic esters, like the metallic derivatives of ethyl acetoacetate (Baly and Desch, J., 1904, **85**, 1029; 1905, **87**, 766; Hantzsch, *Ber.*, 1910, **43**, 3049), are characterised by a deep band, and further, that 1 : 1-dimethyl*cyclo*hexane- and *cyclo*hexane*spirocyclo*hexane-3 : 5-diones and their monohalogen derivatives show (Graham and Macbeth, J., 1922, **121**, 2601) strong selective absorptions which are practically identical with the absorptions of their respective sodium salts. The hypothesis proposed (Hantzsch, *loc. cit.*; Graham and Macbeth, *loc. cit.*) to account for the selective effects in these cases is also applicable to the salts of the barbituric acids and their monohalogen derivatives, and to the acids themselves if strongly ionised, for the same type of six-membered "ring" may be produced in all cases by the formation of an internal salt calling into play auxiliary valencies of the metallic (or hydrogen) atom. It was therefore of interest to find that the apparently exceptional behaviour of the barbituric acids was due to an incorrect observation.

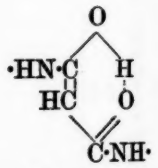


I. Sodium derivative of ethyl aceto-acetate.

II. 3 : 5-Dione compounds and their salts.



III. Sodium derivative of malonic ester.



IV. Barbituric acids and their salts.

Trubsbach (*Z. physikal. Chem.*, 1895, **16**, 711) and Hantzsch (*Ber.*, 1902, **35**, 1006) traced the acidity of barbituric acid to enolisation involving the methylene group, and Wood and Anderson (J., 1906, **89**, 1831) supported this view by showing the almost negligible values of the dissociation constants of *C*-dialkyl barbituric acids compared with the value for the parent compound. It was thought that a series of conductivity measurements would afford confirmatory evidence of the enolic constitutions of the barbituric acids and their monohalogen derivatives and of the existence of the dihalogen compounds in ketonic forms. The method was applied to such substances and also to a series of derivatives of 1 : 1-dimethyl*cyclo*hexane- and *cyclo*hexane*spirocyclo*hexane-3 : 5-diones. Approximate measurements of the hydrogen-ion concentrations of the solutions were in some cases made by the capillator method.

TABLE I.

	$M/100$ in 80% alcohol.	$M/200$ in 40% alcohol.	
	A.	*A*.	*B*.
1 : 1-Dimethyl*cyclo*hexane-3 : 5-dione and derivatives.			
Parent	0·3884	2·792	3·8
4-Bromo-derivative	2·3017	22·590	2·9
4-Chloro-derivative	2·3400	21·310	2·8
4 : 4-Dichloro-derivative	0·1501	0·976	4·2
4 : 4-Dibromo-derivative	0·1694	1·222	4·1
4-Chloro-4-bromo-derivative	0·1953	1·728	4·0
*cyclo*Hexane*spirocyclo*hexane-3 : 5-dione and derivatives.			
Parent	0·4602	2·341	3·9
4-Bromo-derivative	2·3173	21·730	2·8
4 : 4-Dichloro-derivative	0·2148	0·9615	4·2

Columns *A* give the molecular conductivities at 25°, column *B* gives the hydrogen-ion concentrations.

The conductivity measurements were made with unplatinised electrodes. The figures for the molecular conductivities of the dihalogen compounds are not absolute, but maximum, values. This is due to the partial reduction of these compounds to the monohalogen compounds, which occurs on keeping. Direct tests showed that oxidation of the alcohol to aldehyde occurs with the formation of free halogen acid. The change is surprisingly rapid in the presence of platinised electrodes, and it was found possible to reduce the error to a minimum only by using unplatinised electrodes and determining the conductivity as rapidly as possible after making the solution. It is impossible to eliminate the error altogether, as the initial increase in conductivity is very rapid, and the values for the dihalogen compounds are so small that the formation of even traces of the halogen acid and monohalogen compound causes a very considerable percentage increase in the value. A typical effect of the decomposition on the conductivity values is seen in Table II, where the " molecular conductivity " (P) is the value

$$P = scx/R(1000 - x),$$

s being the cell constant, c the number of c.c. containing 1 g.-mol. of substance, R the resistance balanced against the resistance of the cell, and x the balancing length on a 1000-cm. bridge.

The values in Table I show that whereas the introduction of a single halogen atom in the 4-methylene group increases the molecular conductivity considerably, the substitution of halogen for the remaining hydrogen causes a decrease to a value considerably smaller than that of the parent compound; moreover, for the reasons stated, the experimental values for the dihalogen compounds must be considerably greater than the absolute values. It must be inferred, therefore, that whilst in the monohalogen compounds enolisation

TABLE II.

Derivatives of 1 : 1-*dimethylcyclohexane*-3 : 5-*dione*. *M*/100-*Solution in* 80% *ethyl alcohol*.

	P.		
Time (mins.).	4 : 4-Dichloro-.	4 : 4-Chlorobromo-.	4 : 4-Dibromo-.
0	0·1501	0·1953	0·1694
5	0·1968	0·2937	0·2776
10	0·2209	0·3715	0·3434
15	0·2484	0·4272	0·4085
20	0·2646	0·4679	0·4559
30	0·3135	0·5504	0·5362
45	—	0·6521	0·7205
60	0·4271	0·7439	0·9980

is greatly increased, in the dihalogen compounds the reverse obtains and the diketonic structure indicated by the absorption spectra of the compounds is supported.

Similar considerations hold good for the barbituric acids examined :

	M/100 in water.		*M*/200 in water.		*M*/1000 in water.	
Acid.	*A*.	*B*.	*A*.	*B*.	*A*.	*B*.
Barbituric	31·463	3·1	50·468	3·5	104·3	3·7
Dibromobarbituric ...	6·710	3·8	9·3305	3·9	20·28	4·0

	M/500 in 50% alcohol.	*M*/1000 in 25% alcohol.
	A.	*A*.
1-Phenylbarbituric	31·210	80·517
1-Phenylbromobarbituric ...	34·904	68·117
1-Phenyldibromobarbituric ...	3·450	9·242

A = molecular conductivity; *B* = hydrogen-ion concentration.

One of us (W. B. O.) expresses his indebtedness to the Department of Scientific and Industrial Research for a grant which enabled him to participate in the work.

DURHAM COLLEGES,
UNIVERSITY OF DURHAM.

QUEEN'S UNIVERSITY,
BELFAST

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CIX.—*The Properties of the Chlorides of Sulphur. Part I. Freezing Points.*

By THOMAS MARTIN LOWRY, LAURENCE PATRICK MCHATTON, and GRIFFITH GLYN JONES.

THE fact that the chlorination of sulphur takes place in two stages, giving rise first to an orange and then to a red product, was recorded by Berthollet in 1807. It was confirmed in 1832 by Dumas, who analysed the two products and showed that the composition and

vapour density of [liquids which were saturated with sulphur and with chlorine respectively agreed with those calculated for compounds of the formulæ S_2Cl_2 and SCl_2. The view has, however, been held persistently (*e.g.*, by Rose in 1831, on account of the variable composition of the red product, by Isambert in 1878, on account of its variable vapour pressure, and by Ogier in 1883, on account of its small heat of formation) that the " dichloride " does not exist as a definite chemical compound, but is merely a solution of chlorine in the monochloride. In recent years, the existence of a higher chloride of sulphur has been generally admitted; but it has been agreed almost universally that this higher chloride (which Dumas had shown to behave towards indigo quite differently from free chlorine) must be regarded as a tetrachloride, the so-called " dichloride " being merely a mixture of sulphur tetrachloride with monochloride. This conclusion is based upon cryoscopic experiments of Ruff and Fischer (*Ber.*, 1903, **36**, 418) and of Aten (*Z. physikal. Chem.*, 1906, **54**, 55, where a full bibliography is given), which showed a sharp maximum in the melting-point curve at −80°, corresponding with the crystallisation of the *monochloride*, and a rounded maximum at −30°, corresponding with the crystallisation of the *tetrachloride*, but no discontinuity which would indicate the crystallisation of a *dichloride*, although Beckmann subsequently froze out a product of this composition (*Z. physikal. Chem.*, 1909, 65, 289).

Aten found this result particularly puzzling, since his observations of vapour pressure and boiling point proved clearly that the composition of the liquid and vapour phases, which became almost identical at the composition of the *monochloride* (but diverged widely on either side of this composition as a result of the very unequal vapour pressures of Cl_2 and S_2Cl_2, on the one hand, and of S_8 and S_2Cl_2, on the other), definitely approached one another again at the composition of the *dichloride*, provided that opportunity was given for the monochloride and chlorine to enter into chemical combination with one another; under the same conditions, however, there were only very feeble indications of any similar approach at the composition of the *tetrachloride*. Aten was therefore obliged to postulate that the equilibrium $3SCl_2 \rightleftharpoons S_2Cl_2 + SCl_4$ had a temperature coefficient which was so large that a product which was almost all SCl_2 at 0° nevertheless deposited SCl_4 at −30°.

In view of the contradictory character of the evidence, and especially of the fact that the introduction of precise physicochemical methods of examination had made the problem of the real existence of sulphur dichloride even more contentious than before, we thought it important (in spite of the obstinately negative

character of the results recorded by Ruff and Fischer, and by Aten) to open up this question again, and in particular to find out whether the freezing points did in fact afford a decisive proof of the non-existence of the dichloride at low temperatures. In the present paper, therefore, we describe the results of a careful redetermination of the freezing-point curve of the chlorides of sulphur over the range from 16 to 70% Cl. This redetermination has revealed, in addition to the main sections corresponding to the separation of the *monochloride* and the *tetrachloride*, a substantial section corresponding to the crystallisation of the *dichloride*, as well as a small loop near the eutectic point, which is attributed to the crystallisation of a *trisulphur tetrachloride* of the formula S_3Cl_4, which has not been prepared before.

EXPERIMENTAL.

General Principles.—The plotting of an accurate equilibrium diagram is only possible if attention is paid to the three conditions discussed below:

(*a*) Ruff and Fischer determined the *final melting points* in sealed tubes of samples containing 51·5—92·4% Cl. In view of the tedious disturbances of equilibrium which may result from partial or complete solidification in such a complex system, we regarded it as essential to determine in every case the *initial freezing point* of the unfrozen sample. Since Beckmann's values for the m. p. and f. p. of his samples differed in some cases by as much as 40°, in spite of their theoretical identity under ideal conditions, this choice is of some importance.

(*b*) Owing to the slowness with which interaction takes place between sulphur monochloride and chlorine, Aten was able to plot b.-p. and f.-p. curves for these mixtures *before and after combination;* but it appears to have been assumed that mixtures of ready-made chlorides of sulphur come to equilibrium immediately. In our experience, this is not the case, since the f. p. of a freshly prepared mixture of sulphur monochloride and sulphur dichloride may differ by 20° from the value recorded finally. The precaution was therefore taken of heating each sample to 100° in a sealed tube in order to establish a definite condition of equilibrium before determining its f. p. It was found that identical f. p.'s were given by unheated samples to which a trace (0·02%) of iodine had been added, but not by samples which had merely been made up in presence of charcoal.

(*c*) Although both Ruff and Fischer and Aten plotted enough points to show the two maxima in the m.-p. curve, their measurements were neither numerous nor accurate enough to reveal the minor breaks in the curve. The discontinuities due to the crystallis-

ation of sulphur dichloride and of trisulphur tetrachloride were only discovered (i) by using a triple thermo-junction, in place of pentane and toluene thermometers, and so reducing the errors of observation to less than 1°; and (ii) by plotting 15 points in a region which contained only one observation, by Ruff and Fischer, of the eutectic temperature of a sample which was not, in fact, of the eutectic composition. The m.-p. curves which had been used to prove the non-existence of the dichloride were thus shown to be wholly imaginary in the region in which this compound actually crystallises out from the melt.

Materials.—Sulphur monochloride was purified by redistillation under 30 mm. pressure from 1% each of dry charcoal and of sulphur. Liquids richer in chlorine were prepared by adding 1% of dry ignited charcoal to the purified monochloride, cooling in ice, and passing in a current of chlorine which had been dried with sulphuric acid and phosphoric oxide. Some samples were prepared by direct chlorination of the monochloride, others by mixing sulphur monochloride with an over-chlorinated sample of " dichloride " containing 70·4% of chlorine, which was kept in a stoppered bottle and analysed from time to time. The analyses were made by weighing out 0·2 g. in a stoppered glass tube, dropping the tube into a flask containing 50 c.c. of distilled water and 5 c.c. of ammonia (*d* 0·880), and boiling for 5 minutes; 10 c.c. of nitric acid (*d* 1·42) were added to the cold solution, which was boiled to remove oxides of nitrogen. After adding 50 c.c. of *N*/10-silver nitrate, and filtering off the precipitated silver chloride, the excess of silver was titrated with *N*/10-potassium thiocyanate with ferric alum as indicator. This method, which gave results agreeing within 0·1%, was found to be much more convenient than Carius's method, and at least equally accurate.

Measurement of Temperature.—The f. p.'s were measured with a triple thermo-couple made from sleeved and silk-covered copper and constantan wire, gauge 32. The junctions were silver-soldered, filed down as much as possible, and enclosed in drawn-out glass tubes; the leads were protected with shellac. The thermo-couples were calibrated at the f. p.'s of water, mercury, chlorine, and ethylene; but the parabolic relation between *E.M.F.* and temperature, which was deduced from these four readings, was checked by observing also the f. p. of hydrogen chloride, and the b. p.'s of chlorine, hydrogen chloride, and ethylene. The temperatures thus recorded were consistent within 0·5°.

Determination of Freezing Points.—The f. p.'s were determined by cooling the sample over liquid air in a test-tube; this was provided with a glass stirrer passing through a closely-fitting glass tube mounted in a cork, which also carried the thermo-couple.

The voltage did not vary with the position of the thermo-couple in the liquid, but this was kept constant in order to secure as much uniformity as possible. The liquid was cooled rapidly to within a few degrees of the expected f. p., and then by half-degrees at intervals of about a minute until solid began to separate. Samples containing *more* than the eutectic proportion of chlorine gave, within 1° from the first separation of solid, an opaque turbidity; the temperature at which this turbidity first appeared was taken as the initial f. p. of the sample; the observation was repeated twice after allowing the turbidity to clear. The turbidity in samples containing *less* than the eutectic proportion of chlorine appeared very irregularly, apparently by reason of the separation of a second liquid phase; concordant f. p.'s were observed, however, when crystallisation was induced by inoculation with a glass rod dipped alternately into the sample and into liquid air. Since there was much overcooling, the temperature at which this crystallisation could be induced *without producing a rise of temperature* was taken as the initial f. p. of the sample.

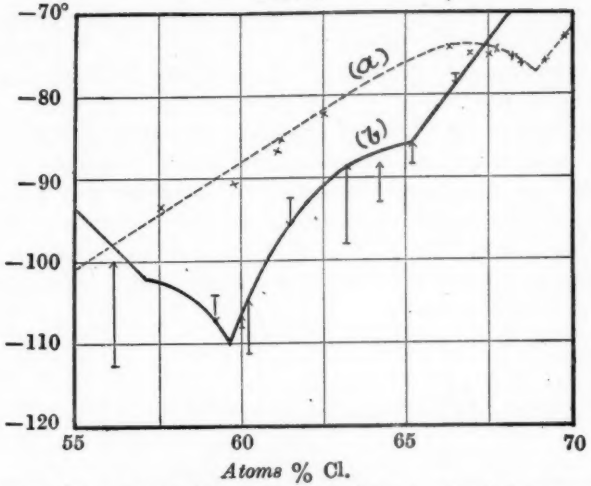
Experimental Results.

(a) *Freezing Points of Freshly Prepared Mixtures of Sulphur Monochloride and Sulphur Dichloride.*—The broken curve of Fig. 1 (*a*) shows the initial f. p.'s of a series of freshly prepared mixtures of sulphur monochloride with an over-chlorinated sample of sulphur dichloride, which had been prepared in presence of charcoal as described above, and contained 68·2 atoms % Cl; three points are also plotted for the same sample of dichloride after further addition of chlorine. Since all these f. p.'s fell to lower values after the mixture had been "aged" for a month in a sealed tube, and still more after heating to 100°, the curve has been drawn through the highest points, lower values being attributed to an approach towards the f. p.'s of the true equilibrium-mixtures.

The curve thus plotted differed from all others hitherto recorded in showing a pronounced maximum at the composition of sulphur dichloride, the real existence of which was thus fully established for the first time by means of f.-p. data. In spite of its very definite character, however, we do not wish to attach any undue value to this curve, since it represents only a particular series of "false equilibria," in which the interaction between the various components of the mixtures is still far from complete. The lower portion of the curve, where the f. p.'s fell below −100°, was regarded as untrustworthy, on account of a tendency for a second liquid phase to separate from the melt in this region, and has therefore been omitted.

(b) *Effect of Preliminary Heating on the Freezing Point of Freshly Prepared Samples.*—The samples used for plotting the f.-p. curve of Fig. 1 (*a*) did not give satisfactory values for the f. p.'s of the final equilibrium-mixtures, perhaps because the repeated manipulation of the samples had allowed too many opportunities for access of moisture. An attempt was therefore made to plot this curve by observing the f. p.'s of mixtures that had been freshly prepared *in presence of charcoal* by the direct chlorination of a sample of sulphur monochloride, under conditions which precluded the access of moisture. The f. p.'s were, however, still quite irregular, until these mixtures also had been heated to 100° in sealed tubes. The

FIG. 1.



(a) *Freezing points of freshly prepared mixtures of sulphur monochloride with sulphur "dichloride" containing 70·4% Cl (broken curve).* (b) *Effect of heating to 100° on sulphur monochloride chlorinated in presence of charcoal (full curve and arrows).*

way in which the f. p.'s of the freshly prepared samples were displaced towards a smooth equilibrium curve by a preliminary heating is shown by the arrows of Fig. 1 (*b*). Although the equilibrium curve is not quite identical with that which was finally plotted, it will be seen that all the f. p.'s approach this curve, whether they were initially above it or below it, although they do not quite reach it in every case. Heating the mixtures *alone* to 100° is therefore far more efficient in producing a condition of equilibrium than mere contact *with charcoal* at atmospheric temperature.

(c) *Influence of Iodine as a Catalyst.*—Since 0·2% of iodine can be used instead of 1% of charcoal as a catalyst to promote the addition of chlorine to sulphur monochloride, experiments were

made on the f. p.'s of heated mixtures to which a trace of iodine (0·02%) had been added, the proportion used being sufficiently minute to avoid the deposition of iodine trichloride on cooling. The results were as follows :

Cl =	68·4	63·1	67·3	68·0	62·2	67·6%.
=	66·1	60·7	65·0	65·7	59·8	65·3 atoms%.
F.p. =	−79·0°	−99·0°	−83·0°	−84·5°	−103·0°	−83·0° (without iodine).
=	−79·0	−98·0	−82·5	−83·5	−103·5	−83·0 (with 0·02% iodine).

No further change of f. p. was produced by the addition of iodine to the heated samples; moreover, identical values were observed when the f. p.'s of unheated samples to which iodine had been added were compared with those of samples (containing no iodine) which had been heated to 100°. It therefore appears that the condition of equilibrium brought about by the addition of iodine at atmospheric temperature is substantially identical with that produced by heating to 100°.

(d) *Freezing-point Curve of Samples previously heated to* 100°.—When a precise method for measuring the f. p.'s had been established, and a satisfactory process had been devised for bringing the sample to a uniform condition, no difficulty was experienced in plotting a f.-p. curve (Fig. 2) in which all the minor details were clearly displayed. The data from which this curve was plotted were as follows :

Cl %.	Atoms %.	F. p.	Cl %.	Atoms %.	F. p.	Cl %.	Atoms %.	F. p.
50·2	47·7	− 83·1°	60·9	58·4	−103·6°	66·3	63·9	−86·6°
51·6	49·1	− 81·5	61·0	58·6	−105·1	66·4	64·0	−87·2
52·1	49·6	− 81·3	61·3	58·9	−107·4	67·1	64·8	−85·9
52·5	50·0	− 79·0	62·1	59·7	−107·4	67·2	64·9	−86·1
55·6	53·1	− 87·0	62·4	60·0	−105·0	67·9	65·6	−82·9
56·1	53·6	− 89·0	63·4	61·0	− 97·6	68·2	65·9	−82·9
58·6	56·1	− 98·4	64·0	61·6	− 95·7	68·2	65·9	−80·0
59·3	56·8	−101·0	65·5	63·1	− 88·6	68·8	66·5	−78·8
59·8	57·3	−103·0	65·5	63·1	− 88·4	70·1	67·8	−73·5
60·1	57·6	−102·6	65·8	63·4	− 88·3	70·6	68·3	−75·0.
60·4	57·9	−103·0						

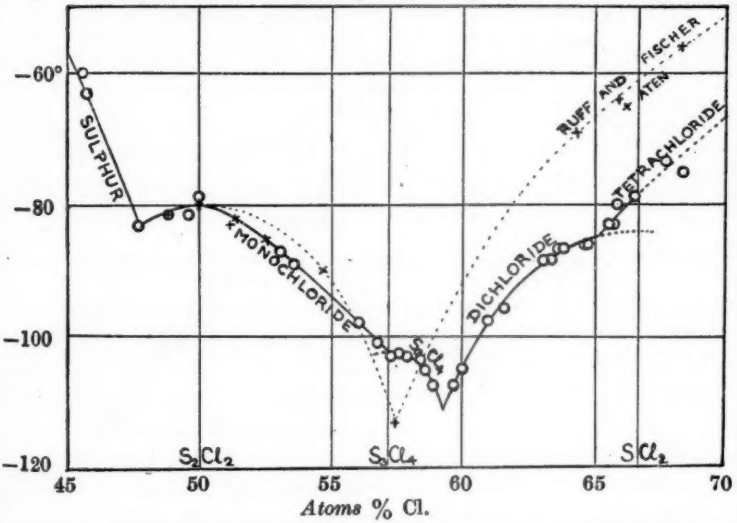
It will be seen that, whereas the broken curve of Fig. 1 (*a*) shows a maximum corresponding with the composition SCl_2, this is not reached in mixtures which had been brought to a condition of equilibrium by heating to 100°, since, after this treatment, *a mixture having the composition of sulphur dichloride deposits crystals of sulphur tetrachloride.*

(e) *Solubility of Sulphur in Sulphur Monochloride.*—In order to carry the equilibrium diagram up to 100% S, measurements were made of the solubility of sulphur in sulphur monochloride. For this purpose sulphur, purified by recrystallisation from toluene,

was added to the monochloride, and heated to a temperature just below the transition point at 96°. The temperatures at which solid sulphur began to separate on cooling the solutions are shown with sufficient exactness in Fig. 3, which covers a much wider range of temperatures than the preceding figures. The temperatures recorded by Aten *for complete dissolution* of sulphur in sulphur monochloride are also shown; as might perhaps be expected, these are considerably higher, since complete saturation is very difficult to attain in presence of a vanishing quantity of the solid phase. It should be noted that, after being heated to 170°, sulphur dissolves permanently in sulphur monochloride, perhaps as the result of the

FIG. 2.

Freezing points of chlorides of sulphur after heating to 100°.



formation of sub-chlorides of sulphur (Ruff and Golla, *Z. anorg. Chem.*, 1924, **138**, 17, 33; Bruni and Amadori, *Atti R. Accad. Lincei*, 1919, [v], **28**, 217), but there is no reason to suppose that this takes place during a short heating at temperatures below 100°.

(f) *Appearance of the Solid Phase.*—The fact that several different compounds may separate in the range from S_2Cl_2 to SCl_4 was confirmed by noting the physical appearance of the solids. Thus:

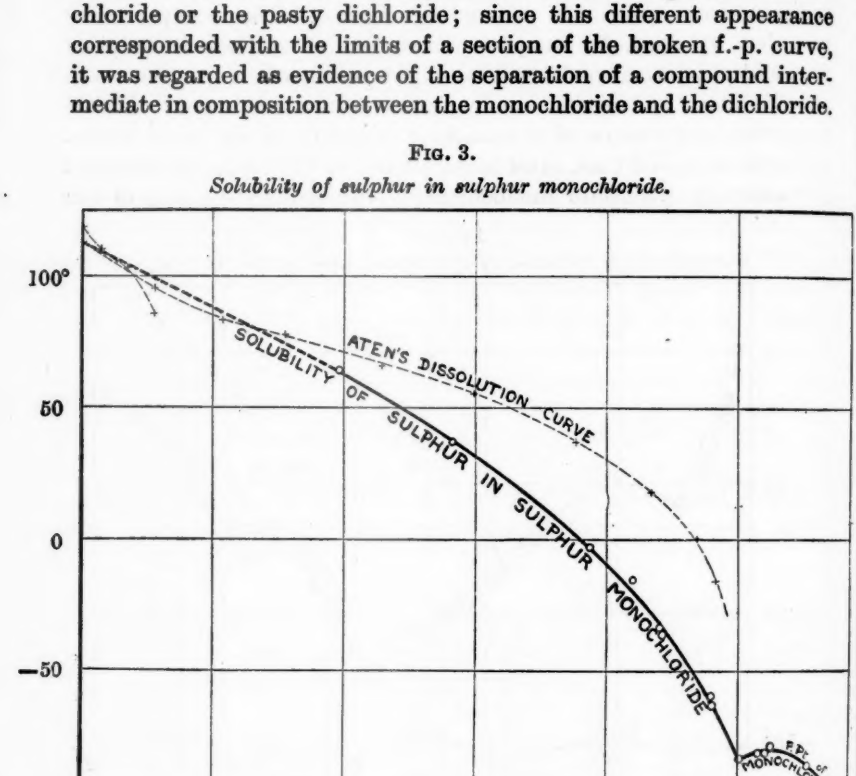
(i) *Sulphur tetrachloride* separated in a buttery form (without overcooling) from mixtures containing more than 67·2% Cl (64·9 atoms %).

(ii) *Sulphur dichloride* separated, again without overcooling, in the form of a finely divided, buff-yellow powder, from mixtures containing 61·6—67·2% Cl (59·2—64·9 atoms %).

(iii) The solid which separated over the narrow range 59·1—61·6% Cl (56·6—59·2 atoms %), after seeding with a sample cooled in liquid air in order to prevent the separation of a liquid phase, was of a flocculent nature, very different from the granular monochloride or the pasty dichloride; since this different appearance corresponded with the limits of a section of the broken f.-p. curve, it was regarded as evidence of the separation of a compound intermediate in composition between the monochloride and the dichloride.

FIG. 3.

Solubility of sulphur in sulphur monochloride.



(iv) Finally, *sulphur monochloride* separated in the usual granular form from mixtures containing less than 59·1% Cl (56·6 atoms %), although these liquids had still to be seeded in order to obtain the true f. p. of the sample.

(g) *Recrystallisation of Sulphur Dichloride.*—Although an equilibrium mixture having the composition of sulphur dichloride deposits crystals of the tetrachloride on cooling, the dichloride forms the solid phase when an over-chlorinated sample of sulphur dichloride is brought back to the correct composition by the addition of sulphur monochloride. Two samples prepared in this way were cooled over liquid air until about one-third frozen; the liquid was

then decanted, and the solid remelted and again partly frozen. On analysis, the final products from a sample containing 69·4% Cl gave Cl = 68·4, 67·3 (calc., 68·9). These results are, of course, merely negative, since they only show that there was no marked change of composition on freezing; but they are of value in that they do not exhibit the striking changes of composition which would be expected if the solid phase were the tetrachloride and not the dichloride. More definite results were obtained by recrystallising the dichloride from light petroleum (b. p. 40°; f. p. −147°). The crystals which separated were drained on an asbestos filter, pressed down with the flattened end of a glass rod, and again drained from the melt. Since the solid always retained some of the solvent, the chlorine and sulphur were both estimated and the percentage composition calculated from the ratio [Found: Cl, (*a*) 68·5, (*b*) 68·0; S, (*a*) 31·5, (*b*) 32·0. SCl_2 requires Cl, 68·9; S, 31·1%].

Discussion.

The equilibrium of the chlorides of sulphur in the middle regions of concentration appears to be dominated by two simultaneous dissociations of sulphur dichloride, proceeding with very unequal speeds:

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2; \quad 3SCl_2 \rightleftharpoons S_2Cl_2 + SCl_4.$$

(i) Since the combination of sulphur monochloride and chlorine is extremely slow at atmospheric temperatures, the first dissociation is probably also slow; the chlorination is, however, known to be catalysed by sulphur tetrachloride, which must therefore also act as a catalyst for the dissociation.

(ii) On the other hand, since sulphur tetrachloride acts as a carrier of chlorine in the chlorination of sulphur monochloride, its interaction with that compound is probably very rapid even at low temperatures (compare $SCl_2 + Cl_2 \rightleftharpoons SCl_4$ which takes place immediately at −75°); moreover, since the dissociation of the dichloride proceeds so far that sulphur tetrachloride actually separates as the solid phase on freezing, this reverse process evidently proceeds with similar speed, so that the second dissociation must be quite rapid.

On this simple basis, we can explain the anomalies now recorded in the f. p.'s of the chlorides of sulphur. In particular, the fact that *sulphur dichloride* separates as the solid phase from a freshly prepared mixture of two liquids, which deposit *sulphur monochloride* and *sulphur tetrachloride* respectively when frozen, is a clear indication that a large yield of the dichloride must have been produced by a rapid interaction of these two compounds, thus:

$S_2Cl_2 + SCl_4 = 3SCl_2$. Moreover, since the f. p., after rising when the two chlorides are mixed, falls again after they have aged, it is clear that the *rapid* reaction by which sulphur dichloride is *produced*, is followed by a *slow* reaction by which it is *destroyed*. This destruction probably depends on a slow dissociation of the excess of sulphur dichloride into monochloride and chlorine according to the equation $2SCl_2 = S_2Cl_2 + Cl_2$; but we are not in a position to assert that this simple and very plausible explanation is in fact correct.

Summary.

(*a*) Samples of sulphur chloride, which have been heated to 100° in sealed tubes in order to bring about a condition of equilibrium, give a f.-p. curve which exhibits not only the familiar maxima due to the crystallisation of S_2Cl_2 and SCl_4, but also two well-defined breaks which are attributed to the crystallisation of SCl_2 and of a *trisulphur tetrachloride*, S_3Cl_4, which has not been prepared previously. The molecular structure of these compounds will be discussed in a subsequent paper.

(*b*) Although an equilibrium mixture having the composition of sulphur dichloride deposits sulphur tetrachloride on freezing, freshly prepared mixtures of sulphur monochloride with an overchlorinated sample of sulphur dichloride exhibit a maximum f. p. at the composition SCl_2, which disappears when the mixture is brought to a condition of equilibrium. This is attributed to a rapid production of sulphur dichloride, followed by a slower process of destruction, perhaps $S_2Cl_2 + SCl_4 = 3SCl_2$ and $2SCl_2 = S_2Cl_2 + Cl_2$.

(*c*) Sulphur dichloride has been frozen out from mixtures freshly prepared as under (*b*), and has been recrystallised from light petroleum by cooling the solution with liquid air.

UNIVERSITY CHEMICAL LABORATORY,
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CX.—*Acid and Salt Effects in Catalysed Reactions. Part VII. The Tridimensional Co-ordination of Catalytic Variables. Relations between the Data for Pure Acids and the Corresponding Minimum-Velocity Mixtures.*

By HARRY MEDFORTH DAWSON.

IT was shown previously (Dawson, this vol., p. 213) that the reaction velocity (u) attributable to the action of the hydrogen and acid ions in solutions which contain an acid–salt mixture of the type

cHA + xMA (c constant, x variable) is connected with the hydrogen-ion concentration by an equation which may be written

$$u = u_i(n + 1/n)/2 = u_i([H^+]/[H^+]_i + [H^+]_i/[H^+])/2 = u_i(10^{\Delta p_H} + 10^{-\Delta p_H})/2 \quad . \quad . \quad . \quad (1)$$

where n is the reduced hydrogen-ion concentration, $[H^+]_i$ and u_i are respectively the hydrogen-ion concentration and the ionic reaction velocity characteristic of the minimum-velocity mixture having the same acid concentration, and $\Delta p_H = \log_{10} n$ is the reduced p_H value of the solution in question.

Since $[H^+]_i$ and u_i vary with the concentration of the acid, the complete representation of the catalytic relations for all possible mixtures of an acid and its salts involves the tridimensional co-ordination of ionic reaction velocity, hydrogen-ion concentration, and concentration of the acid.

If the velocity and p_H co-ordinates (Dawson and Dean, J., 1926, 2872) are combined with a third on which the acid is measured directly by its molar concentration, we obtain a u–p_H–c catalytic model which consists essentially of a catenary surface. Sections parallel to the u–p_H plane give simple catenary curves. The projection on the u–c plane of the points which correspond with a fixed value of n, *i.e.*, with the same reduced hydrogen-ion concentration, gives a series of parabolic curves, as may be seen by writing equation (1) in the form

$$u = \sqrt{(k_h - k_m)k_aKc} \,.\, (n+1/n)$$

for, according to this, the ionic reaction velocity is directly proportional to the square root of the acid concentration.

The corresponding projection on the p_H–c plane gives curves of an exponential type, for, since $[H^+] = n[H^+]_i = n\sqrt{k_aKc/(k_h - k_m)}$, it follows that

$$p_H = \tfrac{1}{2}\log (k_h - k_m)/k_aK - \log n - \tfrac{1}{2}\log c$$
$$= \text{constant} - \tfrac{1}{2}\log c.$$

If the co-ordinates u, p_H, and c are replaced by $\log u$, p_H, and $\log c$, the loci of points corresponding with the same reduced hydrogen-ion concentration will be represented by straight lines in both the $\log u$–$\log c$ and the p_H–$\log c$ planes. For the relations in the $\log u$–p_H plane, we obtain from equation (1)

$$\log u = \log u_i/2 + \log (n + 1/n) \quad . \quad . \quad . \quad (1A)$$
$$\text{or } \log u = \log u_i + \log \cosh \log_e [H^+]/[H^+]_i$$

which is by no means a simple curve for hydrogen-ion concentrations which are not far removed from that which characterises the minimum-velocity mixture, *i.e.*, for values of n lying between

10 and 0·1. On the other hand, it may be noted that for larger and smaller values of n, equation (1A) becomes

$$\log u = \log u_i/2 \pm \log n \quad . \quad . \quad . \quad . \quad (1B)$$

which represents a pair of straight lines, which are inclined to the p_H axis at an angle of 45° and intersect at a point for which the ordinate is represented by $\log u_i/2$. These straight lines obviously correspond with conditions in which the catalytic effect is determined almost entirely by the hydrogen ion, on the one hand, or by the acid ion, on the other.

In some recent experiments on ester hydrolysis in buffer solutions, Karlsson (*Z. anorg. Chem.*, 1925, **145**, 1) has investigated the dependence of the rate on the value of p_H. By plotting empirically the logarithm of the measured velocity coefficient against p_H, he obtains two symmetrically disposed straight lines as the locus of his experimental points provided that these are not closer to the minimum than about 0·7 p_H unit. The fact that the point of intersection of these lines does not correspond with the result indicated by equation (1B) is in all probability due to the circumstance that Karlsson has omitted to take account of the catalytic effects which are produced by the constituents of the buffer solutions other than the hydrogen and hydroxyl ions.

In view of the desirability of including the entire series of p_H values, it seems probable that the most convenient space model for the representation of catalytic relations is that afforded by the use of the co-ordinates u, p_H and c. A model of this kind is illustrated in the accompanying diagram, which has been constructed from data for c values lying between 0·01 and 0·36 N and therefore falling within the range of acid concentrations for which the catalytic effect of acetic acid–sodium acetate mixtures in the acetone–iodine reaction has been actually investigated. The u and p_H axes are in the plane of the paper and the c axis runs from front to back.

In explanation of the model, it should be pointed out that the catenary surface has a definite boundary on the left-hand side. For a given acid concentration, the catenary cross-section terminates at a point which corresponds with the salt-free solution of the acid. Such points for $c = 0{\cdot}01$ and $c = 0{\cdot}04$ are indicated on the photograph by $(u_0)_{.01}$ and $(u_0)_{.04}$, respectively. The projection of these terminal points on the u–p_H plane gives an exponential curve corresponding with the equation

$$u_0 = (k_h + k_a - k_m)10^{-p_H}, \quad . \quad . \quad . \quad . \quad (2)$$

In the u–c plane, the projection is represented by a parabolic curve.

The model suggests that the catenaries become narrower as

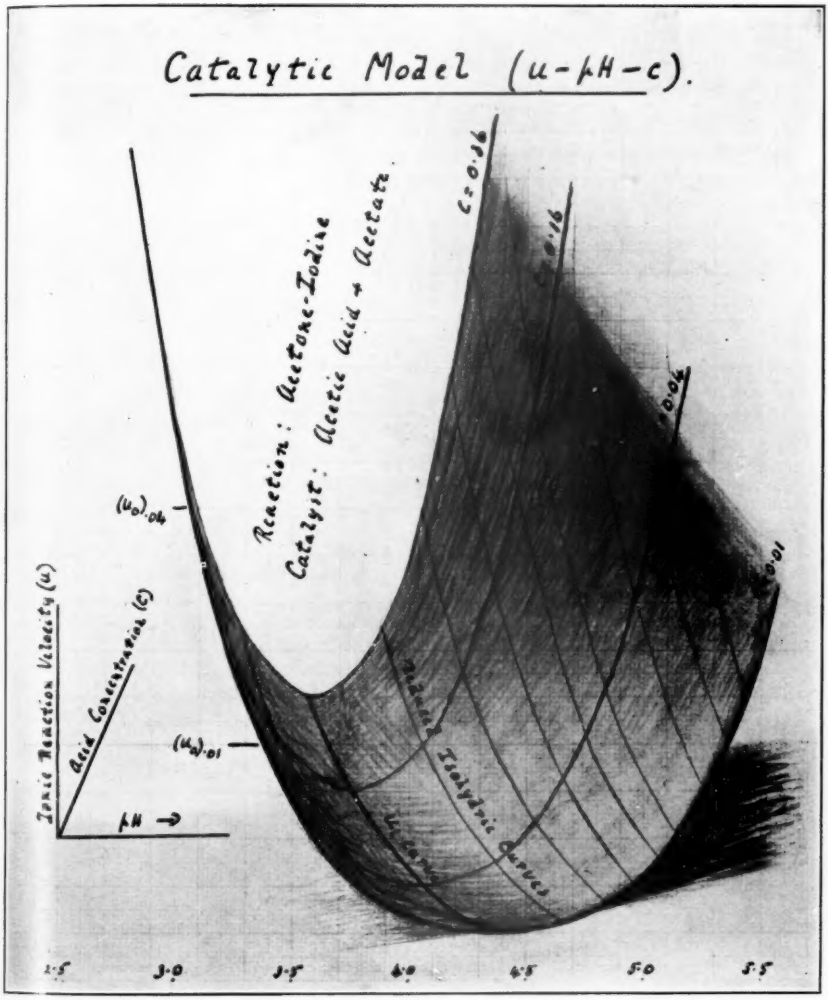


Illustration of the connexion between catalytic activity, acid concentration, and p_H *value.*

[*To face page* 758.]

the concentration of the acid increases. This is true in a certain sense, but it should be noted that the breadth of each catenary at the level of its terminal point on the pure acid side is the same for all catenary cross-sections in that this breadth is measured by $2 \log n_0$, where n_0 depends on the nature of the acid but is independent of its concentration. It has been shown in fact (Dawson, *loc. cit.*, p. 217) that both $n_0 = [H^+]_0/[H^+]_i$ and $r_0 = u_0/u_i$ are independent of c, and since $u_i = 2\sqrt{(k_h - k_m)k_a K c}$, it follows that $u_0 - u_i$ will increase with c and therefore that the catenaries will become extended in the vertical direction as the concentration of the acid increases. This is clearly shown in the diagram.

The lines drawn across the catenary surface from front to back represent approximately the loci of points which have the same reduced hydrogen-ion concentration (n); such points may be described as reduced isohydric points.

To convert the u–p_H–c model into a v–p_H–c model, every point would have to be raised in the vertical direction by $k_m c$.

Finally, it may be noted that the space model has a definite termination in the direction of the c axis and that the limiting catenary in the $c = 0$ plane is a catenary which is characteristic of the combined effects of the hydrogen and hydroxyl ions.

Connexion between the Catalytic Constants and the Quantities n_0 and r_0.

In the previous derivation of the relations connecting $n_0 = [H^+]_0/[H^+]_i$ and $r_0 = u_0/u_i$ with the catalytic constants, it was assumed that the acid is weak and that the hydrogen-ion concentration of the pure acid solution is given by $[H^+]_0 = \sqrt{Kc}$. It is now possible to remove this restriction and to show that the relations are applicable to any acid which ionises in accordance with the mass law. For the pure acid, the reaction velocity is given by

$$v_0 = k_h[H^+]_0 + k_a[A^-]_0 + k_m(c - [H^+]_0),$$

and since $[H^+]_0 = [A^-]_0$,

$$v_0 = (k_h + k_a - k_m)[H^+]_0 + k_m c.$$

The ionic reaction velocity is therefore

$$u_0 = (k_h - k_m + k_a) \,.\, [H^+]_0 = (k_h - k_m + k_a) n_0 [H^+]_i,$$

and since

$$u_i = 2(k_h - k_m) \,.\, [H^+]_i$$

we obtain

$$u_0/u_i = (k_h - k_m + k_a) n_0 / 2(k_h - k_m) \quad . \quad . \quad . \quad (3)$$

Since, further,

$$u_0/u_i = (n_0 + 1/n_0)/2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

it follows that

$$n_0(1 + 1/n_0^2) = n_0[1 + k_a/(k_h - k_m)]$$

whence $$n_0 = \sqrt{(k_h - k_m)/k_a} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and by substitution in equation (3) or (4)

$$r_0 = u_0/u_i = (k_h - k_m + k_a)/2\sqrt{(k_h - k_m)k_a} = [\sqrt{(k_h - k_m)/k_a} + \sqrt{k_a/(k_h - k_m)}]/2 \quad . \quad . \quad . \quad (6)$$

Equations (5) and (6) are identical with those obtained previously on a restricted basis. They will now be examined with reference to the data which have been obtained for acetic acid as catalyst in the acetone–iodine reaction.

The relevant numbers which refer to 25° and to an acetone concentration of 20 c.c. per litre are collected in Table I. The measured velocities v_0 have been obtained by Mr. A. Key for another purpose. The values of u_0 are given by $u_0 = v_0 - k_m c$. The u_i and $[H^+]_i$ values are those recorded by Dawson and Hoskins (J., 1926, 3166), and the $[H^+]_0$ values are derived from $[H^+]_0 = \sqrt{K(c - [H^+]_0)}$ with $K = 1{\cdot}85 \times 10^{-5}$.

TABLE I.

c.	$u_0 . 10^6$.	$u_0 . 10^6$.	$u_i . 10^6$.	u_0/u_i.	$[H^+]_0 . 10^4$.	$[H^+]_i . 10^4$.	$\frac{[H^+]_0}{[H^+]_i}$.
0·01	0·216	0·201	0·041	4·90	4·22	0·47	9·0
0·05	0·512	0·437	0·089	4·91	9·52	0·93	10·2
0·1	0·762	0·612	0·123	4·97	13·5	1·32	10·2
0·2	1·170	0·870	0·164	5·30	19·2	1·90	10·1
0·5	2·10	1·35	0·270	5·00	30·4	3·05	10·0
[1·0	3·25	1·75	0·44	4·0	43·0	5·90	7·3]

Except in the case of the most concentrated acid solution, which shows very markedly the disturbing effects which have been attributed to complex-ion formation, it is apparent that the constancy of the ratios $[H^+]_0/[H^+]_i$ and u_0/u_i is as good as could possibly be expected. Taking $k_h = 465 \times 10^{-6}$, $k_a = 4{\cdot}5 \times 10^{-6}$, and $k_m = 1{\cdot}5 \times 10^{-6}$, the value of u_0/u_i according to equation (6) is 5·13, whilst the value of $[H^+]_0/[H^+]_i$ according to equation (5) is 10·15. The relations between the data for the pure acid solutions and the corresponding minimum-velocity mixtures are thus in satisfactory agreement with the theory over the concentration range $c = 0{\cdot}01$ to $c = 0{\cdot}5$. It is, of course, recognised that the nature of the equations in question is such that the data for an acid for which k_h is not so large compared with k_a or k_m would furnish a more interesting test of their validity, but such data are not yet available.

Summary.

The spatial co-ordination of catalytic variables is considered and the characteristic features of a model, constructed on the basis

of ionic reaction velocity, p_H, and acid concentration co-ordinates, are described.

A general proof is given of the equations which connect the catalytic coefficients k_h, k_a, and k_m with the hydrogen-ion concentrations and the ionic reaction velocities for solutions of the pure acids and of the corresponding minimum-velocity mixtures.

The experimental data for the catalytic effects produced by acetic acid in the acetone–iodine reaction are shown to be in close agreement with these equations over the acid concentration range $c = 0{\cdot}01$ to $c = 0{\cdot}5$.

THE UNIVERSITY, LEEDS. [*Received, February 18th*, 1927.]

CXI.—*Photochemical Equilibrium in Nitrogen Peroxide. Part I.*

By RONALD GEORGE WREYFORD NORRISH.

IN the course of a series of photochemical investigations with different gases, it was discovered that when nitrogen peroxide is enclosed in a water-jacketed vessel and illuminated by the rays from a quartz mercury-vapour lamp, a considerable increase of pressure is developed which is too great to be attributed to the heat effect of the absorbed radiation. For instance, with a total pressure of only 8·5 mm. of nitrogen peroxide, a pressure increase of about 3·3 mm. was obtained. For higher pressures of nitrogen peroxide, this pressure increase rapidly approached a maximum constant value of about 11·45 mm.

The development of this pressure under illumination started rapidly, but became slower and slower until it was complete in about 15 minutes: on being screened from the light, the gas gradually returned to its former pressure, at first rapidly and then more slowly, in the course of about 60 minutes (see Fig. 1).

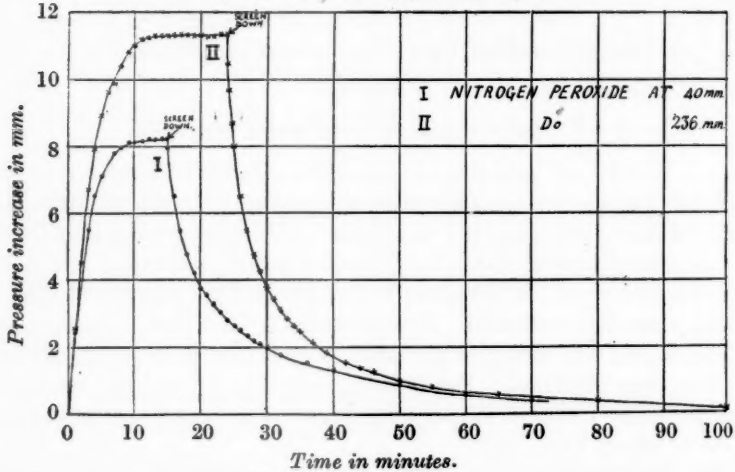
It is well known that nitrogen peroxide is a mixture of two constituents, N_2O_4 and NO_2, in equilibrium with each other. The work of Bell (*Amer. Chem. J.*, 1885, **7**, 32) and of Liveing and Dewar (*Proc. Roy. Soc.*, 1889, **46**, 222) on the absorption of light by nitrogen peroxide at different pressures and temperatures leaves no doubt that the coloured constituent is the NO_2 molecule, whilst N_2O_4 (over the range of the spectrum passed by glass, at any rate) is quite non-absorbing. When the light from the mercury lamp was filtered through a plate of glass 5 mm. thick, the maximum pressure increase was only diminished by a small amount which could be partly accounted for by the loss of intensity due to reflexion at the two

glass surfaces (see Part II); it was therefore concluded that the photoactive constituent of nitrogen peroxide is the NO_2 molecule. The graph of the maximum pressure increases developed in nitrogen peroxide at various total pressures is shown in Fig. 2.

It was at first thought that the pressure increase might be explained on the basis of a shift in the equilibrium $N_2O_4 \rightleftarrows 2NO_2$ under the influence of the light, but the slow recovery of the gas after the light had been shut off is in disagreement with this, since Argo (*J. Physical Chem.*, 1914, **18**, 438) has shown that the above equilibrium is attained instantaneously.

FIG. 1.

Effect of light on pressure of nitrogen peroxide.



Another possibility was that the results might be explained on the basis of the establishment of a photochemical equilibrium of the nature

$$2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2NO + O_2 \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

When a steady state is reached under uniform illumination, there would be an equilibrium quantity of nitric oxide and oxygen present in the system, which would recombine according to the termolecular dark reaction investigated by Bodenstein and Lindner (*Z. physikal. Chem.*, 1922, **100**, 87).

In order to test this view, the effect of adding excess of nitric oxide or oxygen to the system was studied. The addition of increasing concentrations of either of these gases would throw back the photochemical equilibrium to a greater and greater extent until the increase of pressure due to photochemical equilibrium

FIG. 2.

Pressure changes in nitrogen peroxide on illumination.

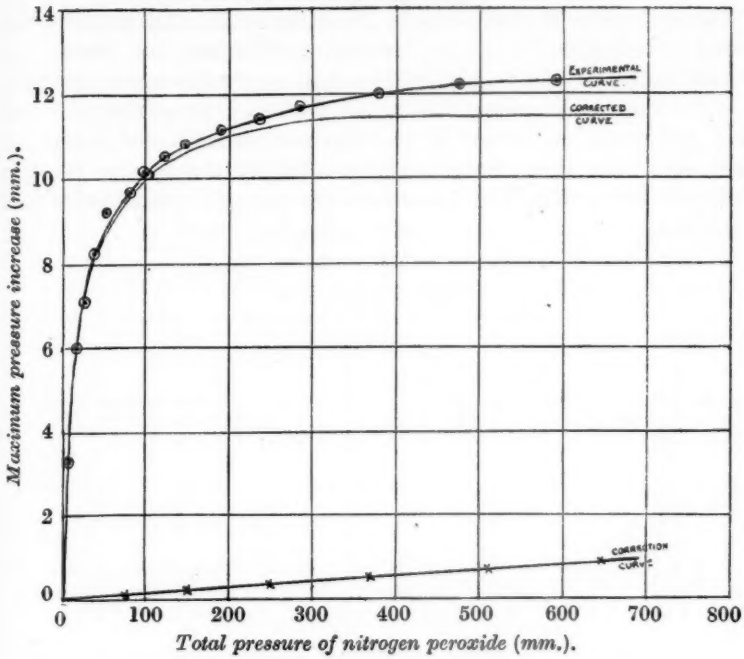
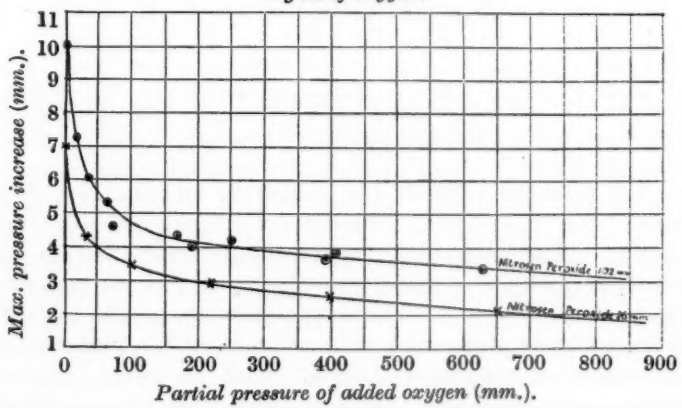


FIG. 3.

Effect of oxygen.



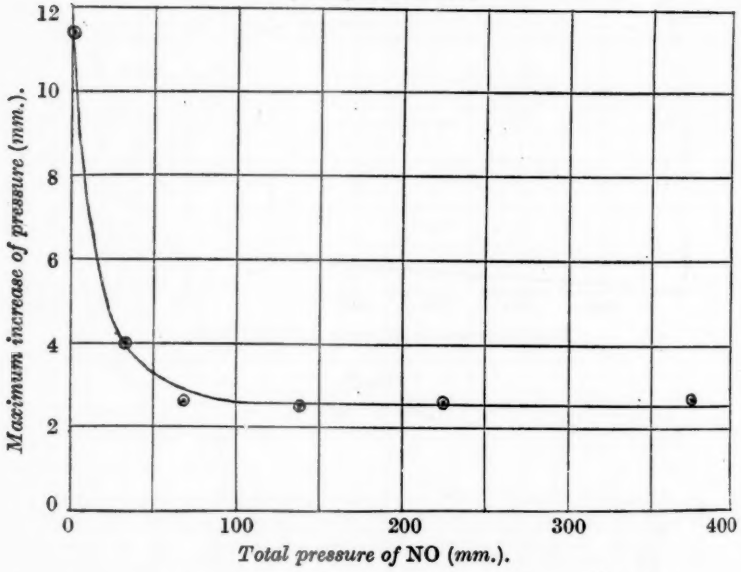
would be very small indeed. This was actually found to be the case (Figs. 3 and 4, Tables III and IV), and in accordance with the fact that the velocity of the reaction $2NO + O_2 = 2NO_2$ depends upon the square of the concentration of nitric oxide, and only on

the first power of that of the oxygen, nitric oxide was found to be the more effective in displacing the equilibrium.

The experiments with excess of nitric oxide and oxygen also showed that after the photochemical equilibrium had been completely suppressed there was still a small residual pressure increase. It will be shown later that this residual effect is proportional to the total light energy absorbed by the nitrogen peroxide, and is suitably ascribed to the sum of the heat liberated by the reverse reaction $2NO + O_2 \longrightarrow 2NO_2$ and the direct heating effect of the absorbed radiation.

FIG. 4.

Effect of nitric oxide.



Granted that the primary photochemical reaction is a decomposition of the NO_2 molecule, the order of the reaction still requires elucidation. A unimolecular reaction would require the liberation of atomic oxygen, and seems improbable in view of the high energy required to effect this. A bimolecular reaction might take place upon the collision of an active with an inactive NO_2 molecule, with the liberation of molecular oxygen. That no atomic oxygen is liberated seems to be proved by the fact that when nitrogen peroxide was illuminated in the presence of hydrogen as a depolariser, no water was formed. The hydrogen indeed slightly decreased the pressure increase (see Table II), but this seems to be simply explained as due to the more rapid loss of heat by the system con-

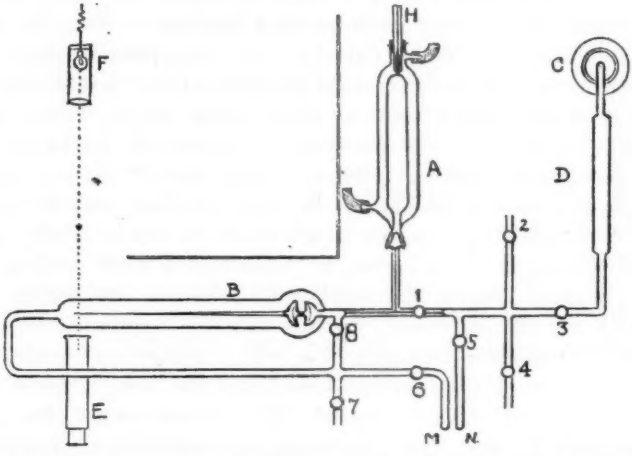
sequent upon the increased conductivity resulting from the addition of hydrogen. It may therefore, for the present, be concluded that the photochemical decomposition of nitrogen peroxide takes place by way of a bimolecular rather than a unimolecular reaction.

It is shown later that the numerical results obtained can be quantitatively explained on the basis of the above hypothesis.

Experimental.

The apparatus employed is shown in Fig. 5. The reaction chamber, A, a double-jacketed clear quartz vessel, was made all in one piece, and through the outer part water at a known temperature (shown by the thermometer H) could be circulated from a

Fig. 5.



thermostat by a pump. The inner part of the vessel A was 18 cm. long and 3 cm. in diameter, and was joined by the ground joint to capillary tubing which communicated with the rest of the apparatus. The pressure changes were measured by the Bourdon gauge B (see Norrish, J., 1925, **127**, 2316), the deflexions of the style of the gauge being observed by a low-power microscope containing a calibrated scale in the eye-piece. A maximum pressure change of about 30 mm. o mercury could be measured by this means to an accuracy of *ca.* 0·05 mm., one scale division corresponding to 0·38 mm. The gauge was surrounded by an outer jacket in which the air pressure could be varied from 0 to 1 atm., thus enabling the total pressure of nitrogen peroxide and other gases which attack mercury to be measured. To effect this the pressure in B was equalised with that in A by means of the stopcock 7, the gauge pointer being brought to zero on the scale, and the pressure of the air was obtained by reading

the vertical mercury manometer, M. By means of the stopcock 8 the pressures in the inside and outside of the gauge could be equalised rapidly, in cases of emergency, to save fracture of the gauge.

The apparatus could be evacuated by way of stopcock 4, which made connexion through calcium chloride and phosphoric oxide drying tubes to a water pump and a Toepler pump, and the pressure could, if desired, be measured directly on a vertical manometer at N.

The nitrogen peroxide after purification was stored in the bulb C, and when not in use was kept in liquid air; when required, it was allowed to melt completely by removing the liquid air, and the vapour was admitted to the evacuated reaction chamber by way of the phosphoric oxide drying tube, D, and stopcocks 3 and 1.

Through stopcocks 2 and 1 pure hydrogen, oxygen, or nitric oxide could be admitted after passing through a series of drying tubes containing calcium chloride and phosphoric oxide. The contents of the quartz vessel were illuminated by a double-barrelled quartz mercury-vapour lamp, of 3000 candle power, with a burner voltage of 150 volts, and carrying a current of 2·5 amps. The lamp was placed vertically beneath and parallel to the reaction vessel A, at a distance of 5 cms. Between the lamp and the vessel A was a horizontal brass screen which could be conveniently opened against the action of a spring by means of a cord working over pulley wheels. When the cord was released the spring automatically closed the screen. In this way, the reaction vessel could be rapidly illuminated or screened at will. A glass screen also could be placed between the reaction vessel and the lamp if desired.

In carrying out an experiment, the reaction vessel, the gauge, and the bulb C were first evacuated as completely as possible by the Toepler pump. Connexion with the pump was then cut off, the nitrogen peroxide was vaporised by the method described, and admitted to the reaction chamber to the required pressure, and stopcocks 3 and 1 were then closed. The liquid-air bath was replaced on the nitrogen peroxide bulb, and the connecting tubes between stopcocks 1, 2, 3, 4, and 5 were evacuated by means of the water pump and washed out several times with any other gas, *e.g.*, pure dry hydrogen, nitric oxide, or oxygen, which could then be admitted to the reaction vessel if required. In the meantime, the lamp had been running for about 10 minutes, in order to reach a steady rate of burning, the screen being closed. The gauge pointer being accurately adjusted to zero, an exposure was now made by opening the screen, and readings of the pressure increase were taken at intervals of about 20 secs. at first, extending to several minutes when the pressure change was completed. When

the maximum pressure increase had been obtained in this way, the screen was closed, and the pressure returned slowly to its original value. It was found necessary to introduce a small and uniform correction into the readings of the pressure changes, due to a slight heating by the lamp of that part of the reaction chamber (*i.e.*, the capillary leads) which was outside the thermostat. This correction curve was determined by observations on the increase of pressure when air at different pressures was enclosed in the reaction vessel; and since the corrections could be determined as accurately as the original measurements themselves, the corrected pressures were of the accuracy (0·05 mm.) already specified. A graph of the actual readings of the pressure change in pure nitrogen peroxide is shown in Fig. 2, together with the correction curve obtained from the measurements on air. The corrected pressure changes themselves are recorded in the tables under the heading "Press. increase (obs.)."

The nitrogen peroxide was prepared by distillation of lead nitrate in a slow stream of oxygen. The evolved gas was passed through a phosphoric oxide drying tube, and condensed by means of a freezing mixture of carbon dioxide and ether. It was fractionated twice in a stream of oxygen, through drying tubes, and finally distilled into the bulb C, and attached to the apparatus (Fig. 5). When cooled in liquid air it froze to a mass of absolutely colourless crystals, which melted to a very pale yellow liquid boiling at 21·5°.

In Table I, the corrected pressure increases for the pure gas are shown; in Tables II, III, and IV, respectively, the results

TABLE I.

Pressure Change in Nitrogen Peroxide on Illumination.

Total press. of nitrogen peroxide, P.	Initial press. of NO_2, p.	Equil. press. of NO_2, p_1.	Press. increase (obs.), n.	Press. increase (calc.), $x + y$.
8·5	7·67	2·8	3·3	3·70
19	15·6	9·4	5·95	5·80
26	20·3	14·2	7·0	6·66
40	28·6	23·1	8·15	7·91
53	35·6	30·3	9·1	8·68
81	58·3	44·4	9·55	9·57
100	56·2	52·4	10·0	9·97
102	56·8	53·2	10·0	9·99
123	64·8	60·7	10·35	10·28
146	72·6	69·3	10·6	10·53
148	73·3	70·0	10·55	10·56
193	87·2	84·7	10·8	10·85
236	99·0	96·6	11·05	11·03
286	111·7	109·6	11·3	11·17
381	133·3	131·2	11·45	11·30
476	152·7	151·4	11·45	11·38
593	173·0	172·1	11·40	11·43

showing the effects of hydrogen, oxygen, and nitric oxide, are given. All pressures are in mm. Hg, and all the experiments were at 20°.

The results of Tables III and IV are plotted in Figs. 3 and 4. From these curves the residual pressure change, remaining after the equilibrium is completely suppressed, can be deduced as described in a later section.

TABLE II.

Effect of Hydrogen.

Nitrogen peroxide at 148 mm. pressure.

Press. of hydrogen ...	0	67·5	174	368	579
Press. increase	10·55	10·15	10·1	10·05	9·8

TABLE III.

Effect of Oxygen.

Press. of nitrogen peroxide, P.	Equil. press. of NO_2, p_1.	Initial press. of O_2.	Total press. change (obs.), n.	Total press. change (calc.), $x + y$.
102	53·2	0	10·0	10·0
102	54·6	17	7·25	6·92
102	55·3	36	6·05	5·76
103	56·1	64	5·3	5·00
102	55·9	73	4·55	4·85
103	56·6	169	4·35	4·02
102	56·3	191	4·0	3·91
100	55·3	254	4·2	3·68
102	56·5	394	3·69	3·44
103	56·7	409	3·85	3·43
102	56·6	631	3·35	3·22
26	13·3	0	7·0	6·56
26	17·7	33	4·3	3·64
26	18·1	101	3·45	2·66
26	18·6	221	2·9	2·21
26	18·9	399	2·55	2·00
26	19·4	655	2·1	1·84

TABLE IV.

Effect of Nitric Oxide.

Press. of nitrogen peroxide, P.	Equil. press. of NO_2, p_1.	Initial press. of NO, P_{NO}.	Total press. change (obs.), n.	Total press. change (calc.), $x + y$.
236	96·5	0	11·4	11·40
235	97·5	28	4·0	5·10
233	97·5	68	2·6	3·14
233	97·5	137	2·5	2·93
233	97·5	249	2·6	2·84
233	97·5	373	2·65	2·82
446	146	249	2·84	3·0
19	15·6	222	0·95	1·03

Theoretical Treatment.

In accordance with the considerations given earlier in this paper, it will now be assumed as a working hypothesis :

(1) That the NO_2 is the photoactive constituent.

(2) That the photodecomposition is bimolecular.

(3) That collision between an active and an inactive NO_2 molecule may result either in chemical change, or in the degradation of the activating energy to heat.

(4) That heat is produced both by the recombination of nitric oxide and oxygen and by the thermal degradation of the absorbed light energy.

The pressure of NO_2 present at each of the pressures used was found by the help of the equation of Wourtzel (*Compt. rend.*, 1919, 169, 1397) for the dissociation constant of nitrogen peroxide,

$$\log K_p/T = -2810{\cdot}5/T + 8{\cdot}9908 \quad . \quad . \quad . \quad (1)$$

which gives $K_p = 71{\cdot}71$ at 20°, the unit of pressure being mm. Hg.

If P be the total pressure of N_2O_4 and NO_2, and p the partial pressure of NO_2, then, at 20°, $p^2/(P - p) = 71{\cdot}71$,

whence $$p = \sqrt{71{\cdot}71\,P + 1285} - 35{\cdot}85 \quad . \quad . \quad . \quad (2)$$

The partial pressures of NO_2 for various total pressures of nitrogen peroxide were calculated by this equation, and a curve was constructed showing the relation between p and P; from this curve the figures shown in the column headed "Initial press. of NO_2" were read off. This pressure of NO_2 present at the start of the experiments has now to be corrected to the pressure obtaining at equilibrium, which will in general be different on account of the photochemical decomposition which has taken place. The correction is relatively large at low pressures, but small at high pressures of NO_2. It is obtained as follows:

If x is the equilibrium pressure increase (exclusive of heating effect) due to the reaction (α) (p. 762), then $2x$ will indicate the equilibrium excess pressure of nitric oxide present in the system. The total nitrogen peroxide present, represented entirely as NO_2, is $2(P - p) + p = 2P - p$. When the photochemical equilibrium is established, this quantity is decreased by the amount $2x$, and if P_1 and p_1 are the new total pressure of nitrogen peroxide and partial pressure of NO_2, respectively, then

$$2P - p - 2x = 2P_1 - p_1 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Also, as before, $$p_1^2/(P_1 - p_1) = 71{\cdot}71 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whence, solving equations (3) and (4), we obtain

$$p_1 = \sqrt{71{\cdot}71P - 35{\cdot}85p - 71{\cdot}71x + 321} - 17{\cdot}93 \quad . \quad . \quad (5)$$

Equation (5) gives the pressure of the photoactive constituent, the NO_2 present when the photochemical equilibrium has been established, from the known values of P and p, and from the value of x

as obtained in a later section. The values of p_1 have been calculated and tabulated in the columns headed "Equil. press. of NO_2" in the tables.

The Photochemical Effect.

We shall now consider the photochemical equilibrium in the nitrogen peroxide. If Y represents the equilibrium concentration of active NO_2 molecules, then their rate of formation, which is proportional to the total light absorbed by the NO_2, may be written

$$dY/dt = k_1 I(1 - e^{-kp_1}) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where I is the intensity of light entering the reaction chamber, and $(1 - e^{-kp_1})$ is the fraction of the photochemically active light absorbed by the NO_2.

The active molecules, according to hypothesis, collide with inactive NO_2 molecules, and cause either thermal degradation or photochemical reaction, the respective coefficients being k_2 and k_3. Thus

$$-dY/dt = k_2 Y p_1 + k_3 Y p_1 \quad . \quad . \quad . \quad . \quad (7)$$

From equations (6) and (7), at equilibrium,

$$Y = k_1 I(1 - e^{-kp_1})/p_1(k_2 + k_3) \quad . \quad . \quad . \quad (8)$$

The rate of photochemical decomposition is therefore

$$k_3 Y p_1 = k_1 k_3 I(1 - e^{-kp_1})/(k_2 + k_3) \quad . \quad . \quad . \quad (9)$$

At equilibrium, this is balanced by the rate of recombination of the products, and if x is the equilibrium pressure increase, as before, and P_O and P_{NO} are the pressures of oxygen and nitric oxide initially present in the system, then the velocity of recombination, according to Bodenstein and Lindner (*loc. cit.*), will be:

$$k_4(P_O + x)(P_{NO} + 2x)^2$$

whence

$$(P_O + x)(P_{NO} + 2x)^2 = k_1 k_3 I(1 - e^{-kp_1})/k_4(k_2 + k_3) \quad . \quad . \quad (10)$$

So long as the light intensity remains constant, as in the present experiments, we may write $k_1 k_3 I/k_4(k_2 + k_3) = K$ and

$$(P_O + x)(P_{NO} + 2x)^2 = K(1 - e^{-kp_1}) \quad . \quad . \quad (11)$$

In the first series of experiments, pure nitrogen peroxide was used; P_O and P_{NO} were therefore zero, hence

$$x = \sqrt[3]{K(1 - e^{-kp_1})/4} \quad . \quad . \quad . \quad . \quad (12)$$

which gives the pressure increase due to photochemical equilibrium and exclusive of the heating effect.

The Heating Effect.

We may now obtain an expression for the heating effect. From equation (7) above, it follows that the heat evolved per second due to thermal degradation is proportional to

$$k_2 Y p_1 = k_1 k_2 I(1 - e^{-kp_1})/(k_2 + k_3) \quad . \quad . \quad . \quad (13)$$

The heat evolved per second by the recombination of the nitric oxide and oxygen is proportional to

$$(P_0 + x)(P_{NO} + 2x)^2 = K(1 - e^{-kp_1}).$$

The total heat evolved per second is therefore proportional to

$$\{k_1 k_2 I/(k_2 + k_3) + K\}(1 - e^{-kp_1}) = K_1(1 - e^{-kp_1}) \quad . \quad . \quad (14)$$

This heat is conducted away at a constant rate, independent of the total gas pressure, for the thermal conductivity of a gas does not vary between pressures of 1 and 760 mm. (Meyer, " Kinetic Theory of Gases "). It therefore follows that there will be a constant equilibrium excess quantity of heat, which we may represent by h, present in the system, and proportional to $K_1(1 - e^{-kp_1})$. The gas will therefore be at a slightly higher temperature than the thermostat, the temperature increment being given by

$$dT = k_5 h/MC_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where M is the total number of moles of gas present in the vessel, and C_v the specific heat at constant volume. If v be the volume of the reaction vessel, then

$$Pv = MRT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

whence, at constant volume,

$$v.dP = MR.dT = k_5 MRh/MC_v \quad . \quad . \quad . \quad (17)$$

Therefore $$dP = k_5 Rh/vC_v = K_0(1 - e^{-kp_1}) \quad . \quad . \quad . \quad (18)$$

where K_0 is proportional to $K_1 k_5 R/vC_v$.

The pressure increase dP due to the combined heating effect of the light and the reverse reaction is therefore proportional to the total quantity of light absorbed. We may represent it by y and write

$$y = K_0(1 - e^{-kp_1}) \quad . \quad . \quad . \quad . \quad . \quad (18A)$$

Determination of the Constants of Equations (11) *and* (18).

For the evaluation of the constants of equations (11) and (18) the data in Table III were used. The total pressure increase, n, is the sum of that due to the reaction, x, and that due to the heating effects, y. With excess of oxygen present the value of the former is

rapidly diminished as the photochemical equilibrium is suppressed, whilst the latter is only slightly changed, since the quantity $(1-e^{-kp_1})$, upon which y depends (equation 18A), alters only to a small extent as x approaches zero (equation 5, x being always small compared with P).

Thus, as increasing quantities of oxygen are added to a given quantity of nitrogen peroxide, the magnitude of the pressure change on illumination approaches asymptotically to the value of y. This is shown quite clearly in the experimental curves (Fig. 3).

When excess of oxygen is present, the initial pressure of nitric oxide being zero, equation (11) becomes

$$(P_0 + x)x^2 = K(1 - e^{-kp_1})/4 \quad . \quad . \quad . \quad . \quad (19)$$

Now p_1 is in general different from p, the pressure of NO_2 introduced into the bulb, on account of the photochemical decomposition which has occurred, and the small correction by which the known values of p are converted to p_1 is obtained from the observed pressure change as follows.

We take the asymptote of the oxygen curve to give y when x approaches zero (*i.e.*, when the photochemical equilibrium is completely suppressed). At this point, equation (5) reduces to $p_1 = p$, and since p is known, K_0 and k can be calculated from the asymptotic values of the two oxygen curves and the known values of p by equation (18A). By this means, using the data in Table III for nitrogen peroxide at 102 mm. and 26 mm., we find $K_0 = 3{\cdot}02$ and $k = 0{\cdot}0267$, the asymptotic values of y being taken as 2·3 mm. and 1·3 mm., respectively.

Approximate values of x required to correct p to p_1 by equation (5) can now be obtained from the observed values of the pressure change (n) by subtracting from them the asymptotic value for y used above. Actually, of course, the value of y changes slowly as x increases, but the total variation in extreme cases is not more than 10%, and the corresponding values of x are not in error by more than 2% when this single value of y is used. The values of p_1 obtained therefrom are not affected to the extent of more than 1% by this approximate treatment, and in most cases by very much less.

From the values of p_1 so obtained, and the constants K_0 and k found above, the values of y for different oxygen pressures are next calculated. These, when subtracted from the observed total pressure change, give the "accurate" observed values of x from which, on substitution in equation (19), we find $K = 2416$. The sums of the calculated values of x and y are shown in Table III and are in good agreement with the observed values for the total increase of pressure.

With excess of nitric oxide present, the photochemical equilibrium is soon almost completely suppressed, the effect being greater than that of oxygen as anticipated (p. 763). Equation (11) now becomes

$$(P_{NO} + 2x)^2 x = K(1 - e^{-kp_1}) \quad . \quad . \quad . \quad . \quad (20)$$

Calculating p_1 as before, and taking the same values for K, k, and K_0, the values of $(x + y)$ have been calculated from equations (20) and (18A) and show suitable agreement with the observed values (Table IV).

Finally, we can now test equation (12), which applies to systems containing no added nitric oxide or oxygen (Table I). Taking the values of K_0, K, and k already found, we have

$$x^3 = 604(1 - e^{-0{\cdot}0267p_1}) \quad . \quad . \quad . \quad . \quad (12A)$$

and
$$y = 3{\cdot}02(1 - e^{-0{\cdot}0267p_1}) \quad . \quad . \quad . \quad . \quad (18B)$$

Hence
$$x^3 = 200y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Also
$$x + y = n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where n is the total observed pressure change. The "observed" value of x can therefore be obtained from the recorded values of n by solving equations (21) and (22), and has been used in equation (5) as before to calculate values of p_1 for the different pressures of nitrogen peroxide used. From these values using equations (12A) and (18B) the values of $(x + y)$ given in the last column of the table have been calculated. It will be seen that close agreement is obtained.

In Table V are shown the experimentally determined heat effects in the presence of excess of nitric oxide or oxygen as described above; the calculated heating effect (y) obtained from equation (18B), putting $p_1 = p$ (since x is negligibly small), is tabulated for comparison. The agreement obtained can leave no doubt that the heating effect is actually proportional to the quantity of light absorbed as is demanded by the theory.

TABLE V.

Heating Effect.

Press. of nitrogen peroxide.	Press. of NO_2 ($p_1 = p$).	Press. change due to heating. (obs.).	Press. change due to heating. (calc.).
19	15·6	0·95	1·03
26	20·3	1·3	1·23
100	56·8	2·3	2·36
233	97·5	2·6	2·82
446	146	2·85	3·00

The close agreement that has been obtained between the observed and the calculated values of the pressure change of nitrogen peroxide on illumination shows that the theory of the change adopted

is in agreement with the facts. It may therefore be definitely stated :

(1) That nitrogen peroxide is decomposed by the light of the mercury-vapour lamp into nitric oxide and oxygen.

(2) That a photochemical stationary state is set up resulting in an increase of pressure in the system.

(3) That the probable mechanism is, first, the activation of an NO_2 molecule, and, secondly, the reaction of this active molecule with an inactive molecule of NO_2 to produce nitric oxide and oxygen.

In Part II of this series the photo-kinetics of this change will be further investigated and discussed.

In the light of these experiments, it is now possible to understand the experiments of Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 72), who found that nitrogen pentoxide is apparently decomposed photochemically by blue light, but only in the presence of nitrogen peroxide, and drew from this the erroneous conclusion that the thermal decomposition of the pentoxide must also be influenced by the peroxide (Daniels, Wulf, and Karrer, *ibid.*, 1922, **44**, 2402). This was disproved by Hirst (J., 1925, **127**, 657) and later by White and Tolman (*J. Amer. Chem. Soc.*, 1925, **47**, 1240), who showed that the thermal decomposition is uninfluenced by the presence of the peroxide.

We may now assume that the photochemical decomposition of nitrogen pentoxide is a secondary dark reaction taking place according to the scheme

$$2NO_2 \xrightarrow{\text{light}} 2NO + O_2$$

$$NO + N_2O_5 \xrightarrow{\text{dark}} 3NO_2.$$

The second reaction, being bimolecular, is more likely to take place than the reverse of the first reaction, which is termolecular, so that the whole of the pentoxide will be decomposed as a result of the photodecomposition of the NO_2.

On this view, it is obvious that the mechanisms of the photochemical and thermal decompositions of nitrogen pentoxide are entirely different, and that no effect on the latter is to be expected in the presence of NO_2, in view of its effect on the former.

Summary.

It has been found that nitrogen peroxide undergoes a marked change of pressure on illumination by mercury light. This pressure change is too great to be accounted for on the basis of a heating effect due to the absorbed light, and has been found to be due (1) to

the establishment of a photochemical equilibrium in the system represented by the equation

$$2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2NO + O_2,$$

and (2) to a heating effect, due to the recombination of the nitric oxide and oxygen and also to the absorbed radiation.

A reaction mechanism involving reaction between active and inactive NO_2 molecules is proposed and is in quantitative agreement with the observed results.

A simple mechanism for the photodecomposition of nitrogen pentoxide is proposed.

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DEPARTMENT OF PHYSICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY. [*Received, December 2nd*, 1926.]

CXII.—*Studies in Polymerisation. Part I. 2 : 3 : 4-Trimethyl l-Arabonolactone.*

By HARRY DUGALD KEITH DREW and WALTER NORMAN HAWORTH.

IN view of the current tendency to regard cellulose, inulin, and possibly starch and other complex polysaccharides as polymerides of anhydrohexose units (Hess and Schultze, *Annalen*, 1926, **448**, 99; H. Pringsheim, *Ber.*, 1926, **59**, 3008; M. Bergmann, *Ber.*, 1926, **59**, 2079), the communication of definite experimental evidence of the molecular association of simple derivatives of the natural sugars is of special interest.

A conspicuous example of the ease of polymerisation of a unit of this nature is furnished by our recent studies of the behaviour of 2 : 3 : 4-trimethyl *l*-arabonolactone (I). This compound, which has hitherto been obtained only in the form of a syrup, is now shown to be crystalline in the pure state (needles, m. p. 45°), and to display a specific rotation +180° in water, as compared with the former value +145° (Pryde, Hirst, and Humphreys, J., 1925, **127**, 355). The crystalline lactone is readily soluble in cold ether and in other organic solvents as well as in water. In the liquid condition, it is hygroscopic, absorbing water with great rapidity on exposure to the atmosphere; in the crystalline state, it displays this property only to a limited extent. Nevertheless, after 2 days' exposure, the crystals change to a liquid which is almost entirely the free mono-

basic acid. It is therefore evident that the monomeric form of the lactone, which contains a simple six-membered ring, is characterised by its high rotatory power, ready fusibility, high solubility, and by the ease with which it is hydrolysed in the presence of water vapour.

When the lactone is kept, however, for some time in an atmosphere containing traces of acetyl chloride vapour or of hydrogen chloride gas, it undergoes a remarkable change. The transformation product is a white powder which is insoluble in ether and sparingly soluble in benzene or other organic solvents. From solution in hot benzene, it separates as a white, colloidal precipitate which, on removal from the solvent, appears as a mass of microscopic, barrel-shaped crystals having a considerably higher melting point (135—138°) than the original lactone (45°). This crystalline transformation product is stable during many weeks in moist air, and the specific rotation in benzene is only about one-fifth of that of the original lactone. The analytical figures indicated that the new product possessed the same or almost the same empirical formula as the simple lactone, whilst it was shown by titration that complete transformation to the sodium derivative of the simple acid occurred after heating for 20 minutes at 100° with a slight excess of $N/10$-sodium hydroxide. With the theoretical amount of alkali this period was not sufficient to effect complete disruption of the complex, thus indicating that the latter is possessed of far greater stability than the simple lactone towards hydrolytic agents.

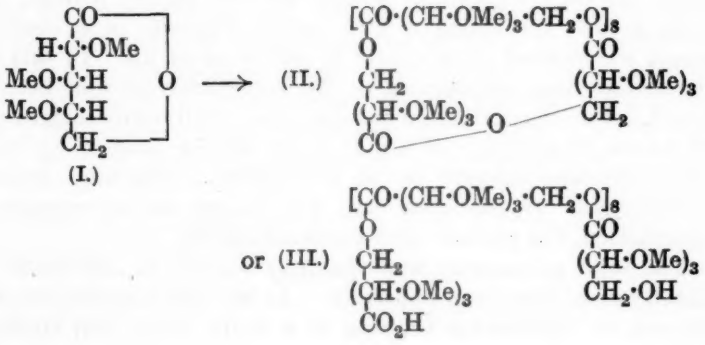
The foregoing evidence, particularly the behaviour towards solvents, pointed unmistakably to the identification of the compound as a polymeride of the trimethyl arabonolactone. This deduction was confirmed by determinations of molecular weight in boiling benzene, which yielded the figures 1900 ($c = 1{\cdot}05$) and 2100 ($c = 2{\cdot}25$). Moreover, it was found that the polymeride could be completely transformed to the simple crystalline lactone by heating to 175° in a vacuum, or by successive treatment with alkali and the equivalent of dilute mineral acid. Indeed, the regenerated lactone solidified even without preliminary distillation, yielding crystals, m. p. 45°, identical with the initial material. There can thus be little doubt that the polymerised product consists of a complex containing about ten associated molecules of the simple lactone $C_8H_{14}O_5$.

The important consideration arises whether the polymerisation occurs as a result of the union of the pre-formed, six-membered rings by the exercise of residual valencies, or whether structural change is responsible for the formation of a long chain or a large ring of carbon and oxygen atoms united only by principal valencies. At present there is no evidence to support the former view, whilst

the properties of the polymeride appear to favour the latter hypothesis. Thus the lower specific rotation of the polymerised compound suggests the elimination of the original six-membered ring and favours the probability of a chain formula in which the lower order of rotatory power may be expected. Again, the much enhanced stability of the polymeride towards moisture would seem to indicate a profound modification of the easily ruptured ring of the initial lactone. So remarkable a change in a simple monocyclic sugar derivative of this nature is unexpected, since earlier examples of such a change have usually been furnished mainly by dicyclic compounds, such as the glucosans. Evidence of the polymerisation of the γ-derivatives of sugars has been adduced, but this has usually been indeterminate in character. We incline to attribute to the new polymeride the formula (II), symbolising a chain of some 50 carbon atoms and 11 oxygen atoms, which may be closed, or which may have the two terminal groups as shown in (III). That a ring structure such as (II) would probably be strainless is conceivable from the work of Ruzicka and his co-workers (*Helv. Chim. Acta*, 1926, **9**, 499).

Analysis fails to decide with certainty between these alternatives, although it may be remarked that the analytical figures correspond more closely with the closed-chain formula (II).

Some evidence of the partial hydrolysis of the polymeride is given by its behaviour in water, in which it is very sparingly soluble in the cold. The hot aqueous solution was feebly acid to litmus, and the acidity did not increase on boiling; and the cooled solution, which deposited only a negligible quantity of the substance, showed a small lævorotation. Evaporation to dryness gave the original polymeride, apparently pure, in the form of broken prisms, m. p. 136—139°. The change to lævorotation after boiling with water may be due to the transformation of the cyclic compound (II) to the open-chain compound (III).



The existence of a crystalline polymeride of this nature, and the simple means by which it can be formed or disrupted, provide a significant commentary on the formulæ which have recently been proposed for cellulose, representing this polysaccharide as polymerised anhydro-glucose, $C_6H_{10}O_5$. Although there remains the possibility that our complex substance may be a mixture of higher polymerides giving an average molecular weight only, yet the crystalline character of the product as revealed under the microscope appears to point to its homogeneity.

Experimental.

2 : 3 : 4-*Trimethyl* l-*Arabonolactone*.—Crystalline trimethyl methyl-arabinoside (m. p. 44°) was hydrolysed by 3% hydrobromic acid, and the product oxidised at 65—70° with bromine. The *lactone*, a viscid, colourless, hygroscopic liquid ($n_D^{15\cdot5°}$ 1·4630), very readily soluble in ether and other organic solvents, solidified to a mass of silky, prismatic needles, m. p. 45° with previous softening. After being drained on porous tile in a vacuum, the product gave: C, 50·7; H, 7·3; OMe, 45·5 ($C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 48·9%). The specific rotation in water ($c = 1·411$) was initially $[\alpha]_{5461}^{21°}$ +206·3°, $[\alpha]_{5780}^{21°}$ +183·5°, $[\alpha]_D^{21°}$ +179·5°; falling after about 4 hours to $[\alpha]_{5461}^{20°}$ +17°. The specific rotation in benzene ($c = 0·86$) was $[\alpha]_{5461}^{21°}$ +203·5°, the solution showing no mutarotation.

Polymeride of 2 : 3 : 4-*Trimethyl* l-*Arabonolactone*.—When the syrupy (unnucleated) lactone was left for some weeks in a closed vessel containing a trace of the vapour of acetyl chloride (and presumably also of hydrogen chloride), it was transformed to a solid, apparently amorphous mass. This was triturated with ether, and after filtration an insoluble, white powder was obtained. The ethereal solution, on evaporation, left a minute quantity of syrup, which was probably the unchanged lactone or an admixture of its lower polymerides. The same polymeride was obtained when the pure crystalline lactone was left during 3 days, along with a tube containing a little acetyl chloride, in a desiccator which was opened occasionally to admit moist air. In this case, the lactone was transformed to the polymeride without becoming liquid. The transformation was also produced (i) by direct treatment of the simple lactone with liquid acetyl chloride, and (ii) by leaving the crystalline lactone in an atmosphere containing hydrogen chloride gas. In the latter case, the change was accompanied by liquefaction, the product afterwards solidifying.

The solid polymeride was sparingly soluble in cold water and slightly more soluble in hot water. At 90°, this solution ($c = 0·39$) showed no appreciable rotation in a 2-dm. tube. On cooling, a

slight opalescence appeared, producing a sediment which was negligible in amount. The solution was slightly lævorotatory, very faintly acid to litmus, and did not reduce Fehling's solution. On evaporation to dryness, the polymeride was recovered quantitatively quite free from oil or other products.

The polymeride obtained by any of the methods already described could be purified from benzene–light petroleum and afterwards from benzene alone. From these solvents, the product separated in colloidal form and afterwards became micro-crystalline; m. p. 135—138°, sintering at about 130° [Found : C, 50·4; H, 7·5; OMe, 46·3; *M*, ebullioscopic in benzene, 1900 ($c = 1·05$), 2100 ($c = 2·25$). The decameric form (II), $(C_8H_{14}O_5)_{10}$, requires C, 50·5; H, 7·4; OMe, 48·9%; *M*, 1900. The open-chain formula (III), $(C_8H_{14}O_5)_{10} + H_2O$, requires C, 50·05; H, 7·4; OMe, 48·5%; *M*, 1918].

Depolymerisation.—The polymeride was quantitatively converted into the simple lactone, $C_8H_{14}O_5$, by heating in a bath at 175° under 0·03 mm. pressure. After the heating had been continued at this temperature for ½ hour, the product distilled, leaving no residue, and completely solidified spontaneously without further purification. The monomeric lactone thus regenerated had m. p. 42° and was identical with the original lactone.

When the polymeride was dissolved in a 50% excess of *N*/10-caustic soda and heated at 100° during 20 minutes, it was completely transformed to sodium trimethyl *l*-arabonate (Found : equivalent of alkali, 8·45 c.c. Calc. : 8·2 c.c.). An amount of *N*/10-hydrochloric acid exactly equivalent to the alkali present was then added, the solution evaporated to dryness at 30° in a vacuum, and the residue extracted with a little cold ether; the syrupy lactone (m. p. 45°) was thus recovered, and this solidified at once on nucleation with the original preparation of 2 : 3 : 4-trimethyl arabonolactone, with which it was shown to be identical by a determination of the mixed melting-point. When the polymeride was dissolved in the exact equivalent of *N*/10-sodium hydroxide (calculated on a simple lactone formula), and the solution heated at 100° during 20 minutes, there remained a 6% excess of alkali, showing that depolymerisation was not quite complete. The specific rotation of the polymeride in benzene ($c = 0·6$) was $[\alpha]^{21°}_{5461}$ +39°, the solution not showing mutarotation.

The authors express thanks to Mr. V. S. Nicholson, B.Sc., for assistance given in this work.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CXIII.—*The Influence of Different Centres of Absorption on the Spectra of Substances.*

By JOHN EDWARD PURVIS.

THE author (J., 1925, **127**, 2771; 1926, 775) has shown that the specific and general absorption of various esters is controlled by the nature and type of the basic and acidic constituents, and, in other substances, by the nature and type of the different absorbing centres in the molecule. The observations have been continued with other esters and substances possessing various centres of absorption.

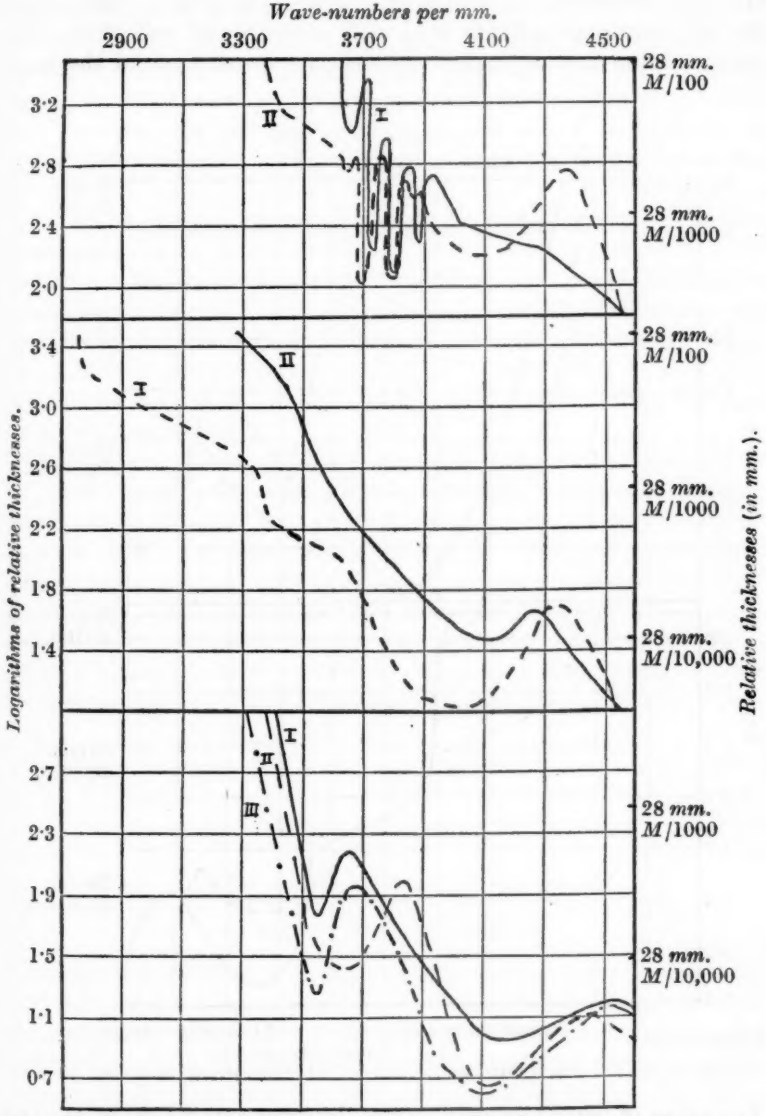
Benzyl Phenylacetate.—The curve (Fig. 1, upper curves) shows the remnants of several benzene bands which are not unlike those of toluene (J., 1915, **107**, 965); and the rapid extension of the rays between $1/\lambda$ 4030 (λ 2480) to $1/\lambda$ 4250 (λ 2352) indicates the remainder of the well-known benzene bands in this region. The author has shown (*loc. cit.*) that these remnant benzene bands occur in phenylacetonitrile, benzyl chloride, benzylidene chloride, and phenylacetic acid, the slight differences being in their position and intensities. In each of these substances the benzene residue retains a certain measure of freedom. Crymble, Stewart, Wright, and Glendinning (J., 1911, **99**, 451) state that phenyl acetate has one moderately weak band at about $1/\lambda$ 3880 (λ 2576). Acetic acid has no band.

Phenylacetaldehyde.—The curve (Fig. 1, upper curves) indicates that this substance also shows some residues of the original benzene bands. In addition, there is a weak acetaldehyde band between $1/\lambda$ 3420 (λ 2923) and $1/\lambda$ 3600 (λ 2777). Acetaldehyde itself shows a band at about $1/\lambda$ 3500 (λ 2856) as first shown by the author and McCleland (J., 1912, **101**, 1810).

Benzoin. Benzoinoxime.—In benzoin, the curve (Fig. 1, middle curves) shows a rapid absorption of the rays towards the red end and a fairly large band at about $1/\lambda$ 4000 (λ 2498), whereas in the oxime this absorption is not so well marked and the band at $1/\lambda$ 4130 (λ 2420) is considerably reduced. These results are comparable with those for benzil as described by Hantzsch and Schwiete (*Ber.*, 1916, **49**, 213), who confirmed the earlier observations of Baly and Stewart (J., 1906, **89**, 502). The benzoinoxime curve is also comparable with those of the benziloximes described by Hantzsch (*Ber.*, 1910, **43**, 1651).

Benzoic Anhydride. Benzoyl Peroxide. Phenyl Benzoate.—The curves (Fig. 1, lower curves) of these three substances, in their general form, are not unlike the curve of benzoic acid, and differ only in strength and position. The author has shown (J., 1915, **107**,

FIG. 1.

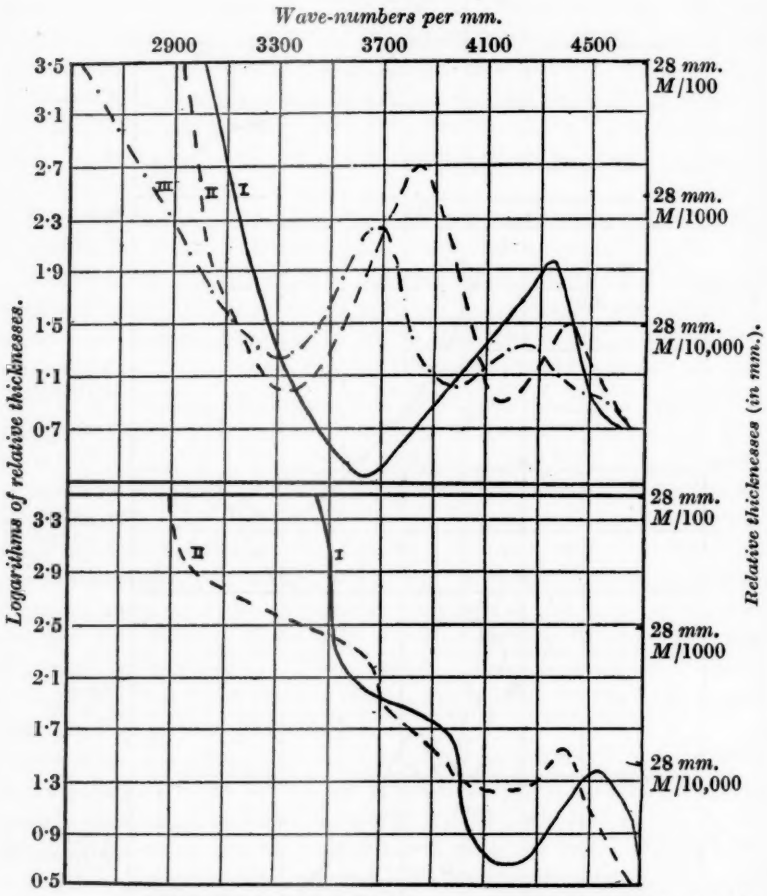


Upper curves: I *Benzyl phenylacetate* (—). II *Phenylacetaldehyde* (— —).
Middle curves: I *Benzoin* (— —). II *Benzoinoxime* (—).
Lower curves: I *Phenyl benzoate* (—). II *Benzoyl peroxide* (— —).
III. *Benzoic anhydride* (— · —).

966) that various benzoates also differ from benzoic acid only in the strength and position of the bands.

Benzyl Salicylate. Benzyl Cinnamate.—Hartley (J., 1888, **53**, 641) first described the two bands of salicylic acid. The author (*loc. cit.*) compared salicylic acid with a number of salicylates, and noticed differences dependent on the nature and type of the base.

FIG. 2.



Upper curves: { I *Benzyl cinnamate* (—). II *Benzyl salicylate* (— —). III *Thiosalicylic acid* (— · —).

Lower curves: I *Phenylurethane* (—). II *Phenylbenzylurethane* (— —).

The curve of benzyl salicylate (Fig. 2, upper curves) shows the two bands of salicylic acid, but there is no appearance of any of the residues of the benzene bands like those which appear in benzyl phenylacetate. Similarly, benzyl cinnamate (Fig. 2, upper curves) shows the strong band of cinnamic acid at $1/\lambda$ 3620 (λ 2760) as first described by Stewart (J., 1907, **91**, 199). In each case, the general

form of the curve is similar to that of the original acid, the slight differences being in position and intensity.

Thiosalicylic Acid.—The curve (Fig. 2, upper curves) is similar to that of salicylic acid, except that the bands are shifted a little more towards the red end, and the line of general absorption is also more towards the red end. Hantzsch and Scharf (*Ber.*, 1913, **46**, 3570) noticed similar differences in a comparison of benzoic and thiobenzoic acids.

Phenylurethane. Phenylbenzylurethane.—The curve of phenylurethane (Fig. 2, lower curves) shows a large band at $1/\lambda$ 4200 (λ 2380). The phenylbenzylurethane shows a weaker band in the same region, but the line of general absorption shifts rapidly towards the less refrangible regions. None of the well-known benzene bands is visible in either substance. Urethane itself gives no absorption bands (Brannigan, Macbeth, and Stewart, J., 1913, **103**, 406) and it is very transparent.

These results, therefore, confirm the author's previous observations of other organic salts and esters in that the absorptive capacity of the basic and acidic parts is modified, and is no longer exactly the same as that of the free base or free acid. The various centres of absorption in any compound, in fact, do not act independently of each other; each centre modifies that of other centres to such an extent that one centre may overpower the influence of the others, as, for example, in the extreme cases of benzyl salicylate and benzyl cinnamate, in which the benzyl bands disappear.

PUBLIC HEALTH CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, November 29th*, 1926.]

CXIV.—*The Glow of Arsenic.*

By HARRY JULIUS EMELÉUS.

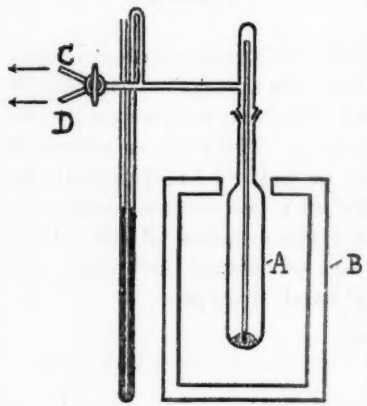
THE glow of arsenic is a feebly luminous and relatively cool flame which is observed in the oxidation of this element just below the ignition point. This mode of combustion differs from normal burning in that heat must be supplied to maintain the flame, which is of such a low intensity that it can be seen only in a dark room. According to Joubert (*Compt. rend.*, 1874, **78**, 1853) the oxygen pressure has to be below a certain value for the occurrence of this phenomenon. Bloch (*ibid.*, 1909, **149**, 775) found the product of the glow to be arsenic trioxide mixed with a little pentoxide. He could detect neither ionisation nor the presence of ozone in the gas passing away from the flame. The experiments described below were made to

investigate the "glow pressure" effect mentioned by Joubert (*loc. cit.*), and to compare this and other features of the oxidation of arsenic with the glow of phosphorus.

Two methods were used. In the first, the rate of pressure change in a closed system, resulting from the condensation of the arsenic trioxide formed, was observed. It was found that during the non-luminous stage of the reaction there was a slow absorption of oxygen, but that when the arsenic was glowing the rate of decrease of pressure was much greater. Secondly, visual observations were made of the temperature at which arsenic began to glow on being slowly heated in a stream of gas under various conditions.

The arsenic was freed from oxide by volatilising the latter in a vacuum at 280°. The element itself was then sublimed at 400°, and the product broken up and sieved between meshes 20—8. About 3 g. were packed round a thermometer bulb in A (Fig. 1), and the apparatus was heated to 300° by a burner, water vapour being removed by a pump attached *via* phosphorus pentoxide guard-tubes at C. Dry oxygen was admitted at D from a cylinder, and the electrically heated furnace, B (10 cm. internal diameter), adjusted to the required temperature, was raised to envelop A. The decrease of pressure per minute was recorded as soon as a contraction began; the pressure was then diminished by a few cm. of mercury, fresh readings were taken, and so on.

FIG. 1.



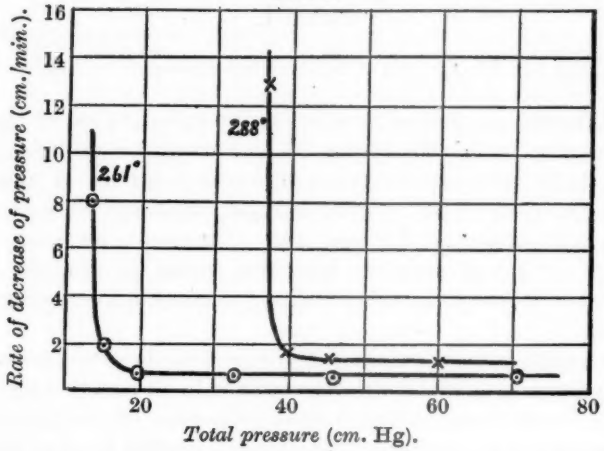
The general nature of the results was as follows. The formation of arsenic trioxide started well below 200°. At temperatures between 250° and 310° the rate of oxidation increased slightly as the pressure was decreased, the reaction being non-luminous. At a certain critical pressure—the "glow pressure"—the rate of oxidation suddenly increased, and a glow appeared near the arsenic surface. Simultaneously the temperature rose by about 7°.

Two experimentally-determined curves are shown in Fig. 2. These illustrate both the break in the oxidation rate and the influence of temperature on its position. From 6 to 10 such sets of observations could be made with one sample of arsenic, provided that this was heated in a vacuum between each set to remove oxide, and that water vapour was excluded. The presence of aqueous vapour

permanently retarded the reaction, probably owing to the formation of non-volatile films on the arsenic grains.

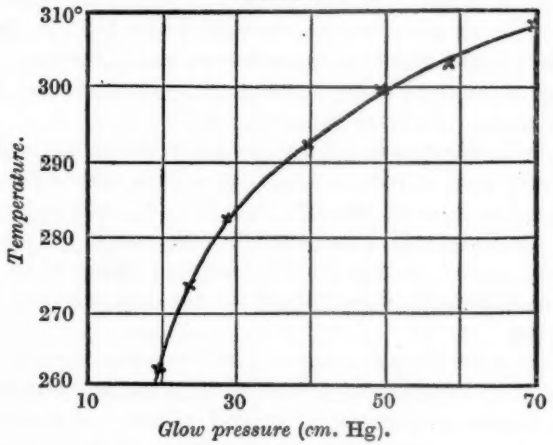
The glow pressure was found to depend both on the temperature

FIG. 2.



and on the length of the tube which was heated in the furnace. The curve in Fig. 3 shows a set of observations illustrating the influence of temperature (the tube was 16 cm. long and of 2·8 cm.

FIG. 3.



internal diameter, 6 cm. being heated in the furnace). In form, this curve corresponds with those obtained by Scharff in studying the influence of temperature on the glow pressure of phosphorus and some of its compounds (*Z. physikal. Chem.*, 1908, **62**, 179).

The length of tube heated was measured from the bottom to the sharply-defined zone where the oxide condensed. Table I shows the effect of varying this distance in a series of experiments. The same tube was used as before, the temperature being 292° ± 1°.

TABLE I.

Length of tube heated (cm.) ...	16	13	10·2	7·2	5·7
Glow pressure (cm. of mercury)	8	14	19	29	38

For different samples of arsenic the observed value of the glow pressure varied by less than 4 cm. This variation is probably due to the very large influence of the conditions of heating. A number of experiments made with oxygen–nitrogen mixtures showed that a glow pressure existed in this case also. The results were not readily compared with one another, however, owing to changes in the composition of the gas mixture during the non-luminous stage of the oxidation.

Experiments in Gas Streams.—The object of these was to compare the temperatures at which the glow started in air and in oxygen, and to find if certain vapours which inhibit the glow of phosphorus have any effect on that of arsenic. Apparatus similar to that shown in Fig. 1 was employed. The preheated gas stream was introduced by a side tube 1 cm. above the arsenic surface, and the temperature was raised slowly until a glow was observed. The main conclusions from these experiments were:

1. The temperature at which the glow appeared increased with the length of tube in the furnace, varying from 210° to 290°. The temperatures were lower than in stationary gas at the same pressure.

2. The glow occurred in oxygen at a temperature about 10° higher than in air under otherwise identical conditions.

3. No effect was produced on the glow temperature if the air used was saturated at room temperatures with carbon tetrachloride or nitrobenzene, or was diluted with 10% by volume of sulphur dioxide. All these substances inhibit the glow of phosphorus, though they are not among the most active. Many of the stronger poisons are thermally decomposed at the temperature at which arsenic glows.

The Cause of the Glow Pressure.—The foregoing experiments show that the glow of arsenic does not occur until the pressure is reduced. The cause of this is indicated in Table I, where it is shown that the greater the distance from the arsenic surface to the zone where the oxide condenses the less readily the glow occurs. From this it appears that the oxide itself hinders the reaction, this effect becoming smaller the steeper the concentration gradient which determines its removal by diffusion. This may be due to retardation of the

reaction owing to the accumulation of its product, or, alternatively, it may be ascribed to a specific inhibitory action, similar to the inhibition of the glow of phosphorus by substances such as ethylene.

The effect of reduction of pressure in promoting the glow may similarly be due to an acceleration of the removal of oxide. It is known that a substance evaporates at a greater rate at low pressures than at high, the relation between the rate of evaporation v, the total pressure P, and the partial pressure of the evaporating substance p', being $v = c \log P/(P - p')$, where c is a constant (Stefan, *Sitzungsber. Akad. Wiss. Wien*, 1873, **68**, 385; compare also Ewan, *Phil. Mag.*, 1894, **38**, 505). The conditions in the present case are similar to those considered by Stefan. Evaluating this expression for the vapour pressure at, *e.g.*, 291°, the relative rate of evaporation is found to increase rapidly below a certain total pressure, as shown in Table II ($p' = 6{\cdot}54$ cms.).

TABLE II.

Total pressure, P (cm. Hg) ...	60	40	20	15	10	8	7
$\text{Log}_{10} P/(P - p')$	0·05	0·08	0·17	0·25	0·46	0·74	1·18

The pressure at which a rapid rate of evaporation sets in depends on the partial pressure of the oxide, and therefore on the temperature. Its variation with temperature is, moreover, similar to that of the glow pressure itself. If the above conception is correct, the production of the glow of arsenic on reducing the pressure may be considered as due, at least in part, to an acceleration of the removal of oxide, and hence of the reaction itself.

Analogy with the Glow of Phosphorus.—The chemical similarity of arsenic and phosphorus extends to their phosphorescent flames. In neither case does the luminous oxidation in oxygen start until the pressure is reduced. In each instance, the higher the temperature the less is the requisite pressure reduction. The non-luminous reaction preceding the glow is, however, much more vigorous for arsenic than for phosphorus (Rayleigh, *Proc. Roy. Soc.*, 1924, *A*, **106**, 1), and the experiments indicated that the ease of removal of the oxide so formed largely determined the occurrence of the glow. No corresponding phenomenon is known in the oxidation of phosphorus.

The glow of phosphorus occurs at considerably higher temperatures in oxygen than in air. In the case of arsenic, these two temperatures were found to be more nearly the same, and the difference could be ascribed to a larger formation of oxide in oxygen. Three substances which inhibit the glow of phosphorus are without influence on that of arsenic. It is possible, however, that others will be found capable of inhibiting the latter reaction also.

The author wishes to express his gratitude to Professor H. B. Baker, in whose laboratory these experiments were carried out, for his interest and advice. The research has been conducted during the tenure of an 1851 Senior Studentship.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, January 18th*, 1927.]

CXV.—*The Origin of the Ultra-violet Spectrum of the Glow of Phosphorus.*

By HARRY JULIUS EMELÉUS and RONALD HERBERT PURCELL.

THE spectrum of the light from glowing phosphorus is continuous in the visible region and shows five groups of bands in the ultra-violet at about λ 3419—3245, 2633—2594, 2552—2527, 2477—2451, 2393—2371 Å.U. (Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235; Petrikaln, *Z. Physik*, 1924, **22**, 119). They have been observed in the normal flame of phosphorus (Emeléus and Downey, J., 1924, **125**, 2491), in the glow of phosphorus trioxide, and in the flame of phosphine (Emeléus, J., 1925, **127**, 1362). The band at λ 3270 was recorded by Hartley (*Phil. Trans.*, 1894, **185**, 168), who introduced phosphorus pentoxide into the oxy-hydrogen flame. These bands were also measured by Geuther in a comprehensive survey of the phosphorus spectra (*Z. wiss. Phot.*, 1907, **5**, 33); he obtained them, together with other bands apparently not present in the glow, on volatilising potassium phosphate in the carbon arc. Other ways of producing what is apparently the same spectrum are described in Kayser's Handbuch (Vol. VI), but from none of these methods can the origin of the bands be determined unambiguously.

The experiments described below consist in an examination of the ultra-violet spectrum of the phosphorescence of phosphorus pentoxide, and of the discharge through its vapour. Ebert and Hoffmann (*Z. physikal. Chem.*, 1900, **34**, 80) found that phosphorus pentoxide exhibited a strong phosphorescence after illumination, especially at low temperatures. They recorded the visible spectrum as continuous, with a maximum intensity in the green, a result which was confirmed in the present work during an unsuccessful search for ultra-violet bands. The discharge through phosphorus pentoxide vapour gave a complex band system, in which were included the bands of the spectrum of glowing phosphorus. Finally, a re-examination of the latter phenomenon was made, revealing other bands common to these two spectra.

The Spectrum of the Phosphorescence of Phosphorus Pentoxide.—The spectrographs used were a Hilger quartz instrument (size E6), for the loan of which the authors are indebted to the Air Ministry, and a large-aperture quartz spectrograph of special construction. This had two lenses working at an aperture of f 4·5 and a Cornu prism of 7·5 cm. base. The dispersion at λ 2550 was approximately 30 Å.U. per mm.

The apparatus used in photographing the spectrum of the phosphorescence at liquid-air temperatures is shown in Fig. 1. Pure phosphorus pentoxide was distilled in a vacuum on to the outer surface of the inner tube, T, from a tube having a ground glass

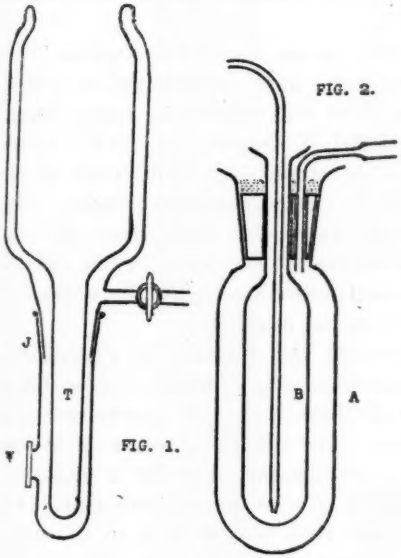


FIG. 1.

FIG. 2.

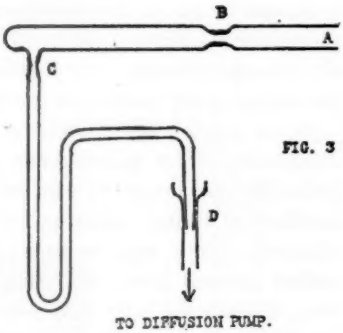


FIG. 3

joint interchangeable with J. The outer tube (shown in position), with a quartz window, W, attached by wax, was then quickly replaced and the interspace was kept exhausted by a diffusion pump. Liquid air was poured into the inner tube, T, as required.

In Fig. 2 is shown a simpler device used for studying the phosphorescence of phosphorus pentoxide cooled to about — 50° by carbon dioxide. The outer tube, A, was of clear quartz, and phosphorus pentoxide was sublimed directly from it on to the inner tube. Cooling was effected by carbon dioxide, which was delivered from a cylinder and passed through a fine jet at the end of a copper tube inserted into the inner vessel.

The relatively feeble phosphorescence at the ordinary temperature was photographed by filling a silica tube with the pentoxide.

Blank experiments were made to examine the phosphorescence of the silica tube itself.

The pentoxide was illuminated in each case by a condensed spark between aluminium poles placed 1 cm. from the apparatus containing the oxide. A jet of water playing on the silica opposite the spark kept the surface clean. A sector, synchronised with the spark, rotated between it and the slit of the spectrograph, placed in alinement. The pentoxide was illuminated by the spark during one-quarter of each revolution of the sector, the speed of which was varied according to the duration of the phosphorescence (which was determined by the temperature). The actual exposure of the phosphorescence was about two-thirds of the period of each revolution.

Exposures of 10—140 hours were made under the various conditions specified; in each case the band in the visible region with a maximum intensity at about λ 4600 was observed, using Ilford Monarch plates (compare Ebert and Hoffmann, *loc. cit.*). There was no evidence of an ultra-violet spectrum. A photograph showing this band is given in Plate 1 (*b*). It corresponds roughly with a broad band in the spectrum of the visible light from glowing phosphorus [Plate 1 (*d*)]. This suggests that the latter is due to the phosphorescence of phosphorus pentoxide under the action of the ultra-violet radiation emitted in the reaction.

Spectrum of the Discharge through the Vapour of Phosphorus Pentoxide.—The phosphorus pentoxide was contained in a silica tube (18 cm. long, 0·8 cm. internal diameter) with a clear end, the method of filling being as follows. The silica apparatus ACD was cleaned, dried, and connected to a diffusion pump by a mercury-sealed ground joint, D. A quantity of pure phosphorus pentoxide was introduced into BA, which was then sealed at A in the oxy-hydrogen flame. The apparatus was exhausted, with the U-tube cooled in liquid air, BC was baked out, and AB warmed. The pentoxide was distilled into BC, and AB was sealed off at the constriction B. After distilling the pentoxide four times from one end of BC to the other with the pump working, in which process much of it was transferred to the U-tube, the constriction C was sealed.

External electrodes of copper foil, with a condenser and spark-gap in the circuit, were used in exciting a discharge through the tube, which was heated electrically to 200°. The discharge was dim, and of a greenish-white colour. Exposures of up to 40 hours were needed on the Hilger spectrograph.

A complex band spectrum was observed, which was compared directly with a spectrogram of the glow of phosphorus taken on the

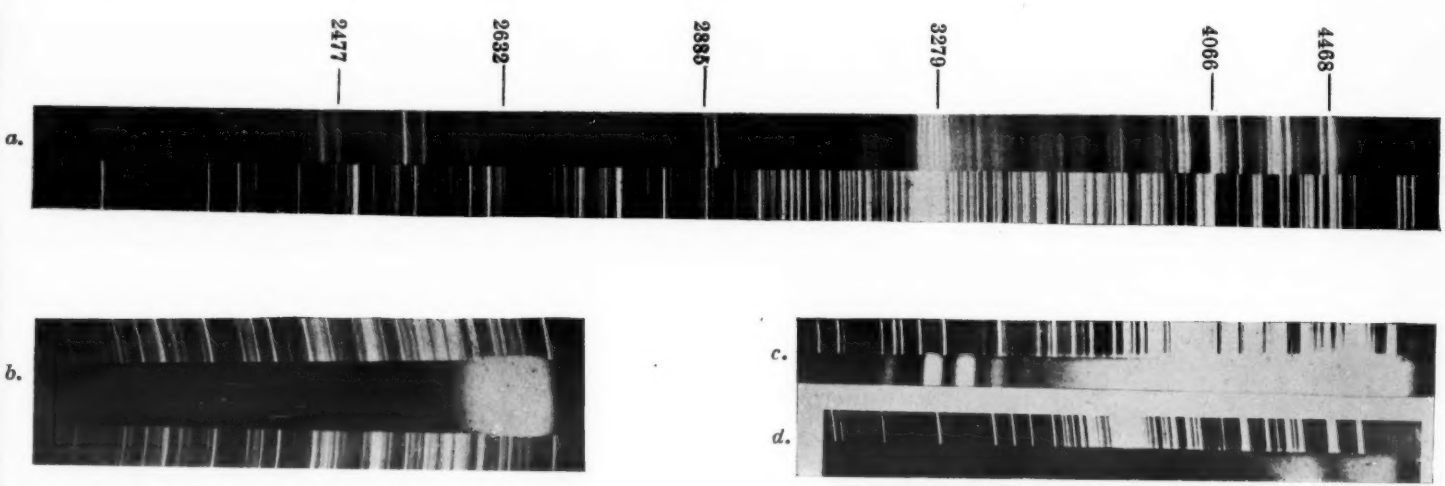


PLATE 1.

(*a*) *Spectrum of discharge through phosphorus pentoxide vapour* (2 *hours*).
(*b*) *Spectrum of phosphorescence of phosphorus pentoxide at* $-55°$ (45 *hours*).
(*c*) *Spectrum of glow of phosphorus* (480 *hours*).
(*d*) *Spectrum of glow of phosphorus on panchromatic plate* (250 *hours*).
Copper-arc reference spectra.

same instrument. There was no doubt that the bands in the glow spectrum were present in the discharge, although in the latter there were many additional bands, and the isolated groups were connected by bands of low intensity. Most were narrow and degraded towards the red. The positions of the violet edges, which were fairly sharp, were measured. In certain cases, where there was no definite head, the approximate position of the violet edge of the band was again ascertained. Plate 1 (*a*) is an enlargement of this spectrum, showing the groups of narrow bands below λ 3000, and also the complex band at λ 3300—3200. Only the more intense band heads above λ 3000 are recorded, the dispersion of the instrument being small. The two narrow bands at λ 2896 and 2885 are attributed to carbon.

Table of Wave-Lengths of Violet Edges of Bands.

λ.	λ.	λ.	λ.	λ.	λ.	λ.
4468 (7)	3493 (4)	3211 (3)	2896 (7)	2689 (2)	2534 (7)	2425 (4)
4346 (9)	3469 (6)	3135 (6)	2885 (8)	2665 (4)	2533 (4)	2421 (2)
4276 (6)	3313 (4)	3129 (3)	2861 (3)	2646 (4)	2526 (2)	2405 (1)
4119 (7)	3303 (4)	3124 (3)	2840 (4)	2632 (4)	2511 (2)	2392 (2)
4066 (10)	3287 (3)	3064 (3)	2823 (4)	2617 (2)	2499 (4)	2380 (3)
3944 (7)	3279 (4)	3045 (4)	2806 (3)	2602 (4)	2488 (4)	2376 (2)
3911 (7)	3270 (6)	3008 (4)	2778 (4)	2593 (5)	2477 (5)	2368 (1)
3747 (6)	3266 (6)	2937 (3)	2762 (4)	2580 (5)	2464 (4)	2353 (2)
3726 (5)	3256 (6)	2921 (3)	2720 (1)	2553 (5)	2445 (6)	2343 (2)
3517 (4)	3246 (6)	2912 (3)	2705 (5)	2546 (4)	2432 (6)	2318 (2)

The error in the measurements below λ 3000 is probably less than 2 Å.U. The bands between λ 2200—2800 and the complex band at λ 3100—3400 appear to correspond in part with the more precise measurements of Geuther, de Watteville, and de Gramont (Kayser, *op. cit.*, p. 253), but the spectra are not identical. This can be ascribed to the low dispersion of the instrument, and the different means of excitation used in the present research. The description of this spectrum does not come within the scope of this paper. It is intended to attempt to correlate it with the absorption spectra of the oxides of phosphorus.

From these results it was concluded that the band spectrum observed in the discharge through phosphorus pentoxide was emitted from the molecule of an oxide, and that the spectrum of the glow of phosphorus had the same origin.

Re-examination of the Spectrum of the Glow of Phosphorus.—The bands described by Geuther (*loc. cit.*) include groups of low intensity at λ 2789—2647, and a group at λ 2320—2280. These and other bands observed in the discharge through phosphorus pentoxide had not been observed in the spectrum of the glow of phosphorus. The large-aperture quartz spectrograph was therefore used in a re-

examination of this phenomenon. The light source was a phosphorus slab cast in a tray (Centnerszwer and Petrikaln, *loc. cit.*).

With an exposure of 480 hours the five groups of bands already known were observed. Some of the negatives showed the components of each group. The continuous spectrum extended to λ 2700, partly obscuring the band at λ 3270. Three new broad bands were also visible, although the component narrow bands of each of these groups could not be distinguished. Their approximate positions were λ 2300—2325; 2660—2700; 2740—2795. Of these new groups, only one (that at λ 2660—2700) has been satisfactorily reproduced in Plate 1 (*c*). They correspond with groups of bands recorded by Geuther, which are also present in the spectrum of the discharge through phosphorus pentoxide vapour, a fact which supports the view put forward as to the origin of the spectrum of the glow of phosphorus. A further exposure of 250 hours on a panchromatic plate showed that the spectrum of the glow of phosphorus extended into the red. What are apparently two broad bands occur at λ 5200—5900, and λ 6000—6800. The dispersion of the instrument is too small to determine if these are due to the merging of narrower bands.

Summary.

Attempts have been made to determine the origin of the spectrum of the glow of phosphorus by unambiguous means. The ultra-violet spectrum of the phosphorescence of phosphorus pentoxide was first photographed, and exhibited none of the bands occurring in the spectrum of the glow of phosphorus. The discharge through the vapour of phosphorus pentoxide in a silica tube gave a complex band spectrum, which included all the bands known in the spectrum of the glow of phosphorus. A re-examination of the latter phenomenon showed further bands common to these two spectra. It was concluded that the ultra-violet spectrum of the glow of phosphorus had its origin in the molecule of an oxide.

We wish to thank Professor H. B. Baker, F.R.S., in whose laboratory these experiments were carried out, for his keen interest and advice. We are greatly indebted to Professor A. Fowler, F.R.S., who has placed facilities at our disposal and advised us in the interpretation of the spectra. We also wish to thank Dr. W. E. Downey, who developed the apparatus and technique used in studying the phosphorescence of phosphorus pentoxide at liquid-air temperatures, for kindly giving us the benefit of his experience. One of us (R. H. P.) is in receipt of a maintenance grant from the Department of Scientific and Industrial Research; the other holds

an 1851 Senior Studentship. Apparatus has been purchased from grants both from the Dixon Fund of the London University and from Messrs. Brunner Mond and Co., Ltd.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, January 18th*, 1927.]

CXVI.—*The Burning of Carbon Disulphide near the Limit for the Propagation of Flame, with some Remarks on the Ignition Point of Sulphur.*

By ALBERT GREVILLE WHITE.

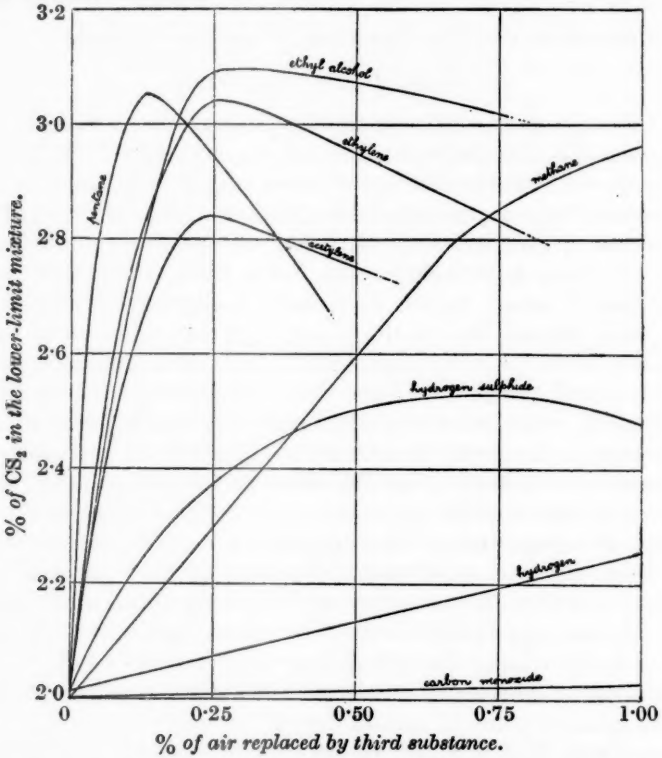
IN a communication on limits for the propagation of flame in mixtures containing air and more than one vapour (J., 1922, **121**, 2561), it was shown that the addition of small quantities of the vapour of ethyl ether, benzene, acetone, or acetaldehyde to carbon disulphide–air caused a pronounced contraction of the propagation range. This was most noticeable at the lower limit, where very small quantities of added vapour *increased* considerably the amount of disulphide present at the limit, although the addition of larger quantities of the vapours reduced the amount of disulphide necessary to give a limit mixture. It was thus found possible to divide the propagation range into two parts, giving four limits instead of the normal two. A similar division for ethyl ether–air is described in the same communication, but this phenomenon relates to the upper limit, near which ether–air mixtures can often propagate a cool flame. It was presumed that propagation at the limit in carbon disulphide–air was catalysed by some product of the combustion, but that this catalysis was inhibited by certain vapours, although not appreciably affected by similar quantities of carbon monoxide, dioxide, or tetrachloride, or of hydrogen.

Phenomena apparently connected with the above were reported on the ignition point of carbon disulphide mixtures by Frankland (*Chem. News*, 1862, **6**, 3), whose work has recently been extended by Dixon (*Rec. trav. chim.*, 1925, **44**, 305), and by Delépine (*Bull. Soc. chim.*, 1922, **31**, 762) for the spontaneous oxidation of certain sulphur compounds in air. Dixon suggests that carbon monosulphide catalyses the phosphorescent combustion of the disulphide, and that the inhibitors act by condensing on the surface of the monosulphide. Delépine found that certain compounds in which sulphur was doubly bound to carbon or phosphorus oxidised in air at the ordinary temperature. This oxidation was apparently stopped by the products of the reaction, and was markedly hindered by traces

of ethyl ether or acetaldehyde, and to some extent by ethyl alcohol and benzene. It was promoted by fixed alkali or ammonia, and also by the lower saturated aliphatic acids. He favoured an explanation similar to that advanced by Moureu and Dufraisse to account for the behaviour of " antioxygens " in autoxidation (J., 1925, **127**, 1), in which the compound first produced is assumed to be a peroxide.

FIG. 1.

Showing the value of the lower limit for carbon disulphide–air when part of the air is replaced by a third substance.



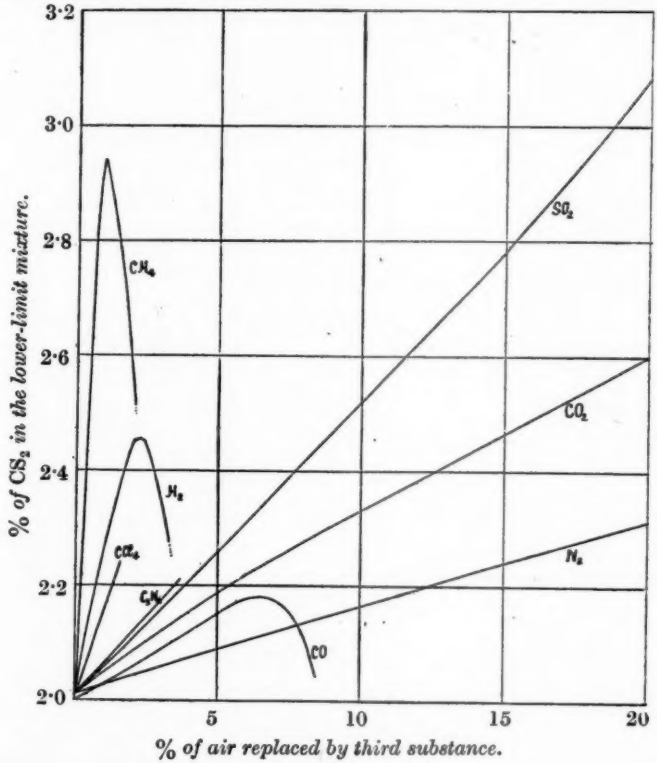
The present work consists largely of an extension of the former results. All limits were determined for downward propagation at the ordinary temperature and pressure in glass tubes 5 cm. in diameter and 150 cm. long. The preparation and ignition of the mixtures were carried out as previously described (J., 1922, **121**, 1244, 2561; 1924, **125**, 2387). Tables I and II show the limits for the propagation of flame in mixtures of various gases and vapours with carbon disulphide and air. All are lower limits except in the one case specified. Compositions are given in percentages by volume.

The calculated limits are those given by Le Chatelier's rule, assuming the values 4·0% and 12·0% for the carbon disulphide limits. The results are shown graphically in Figs. 1 and 2.

The two combustibles present sometimes appeared to burn separately, as two flames were obtained touching only near the axis of the tube. This was well marked for a mixture of carbon monoxide, carbon disulphide, and air containing 7·9% of the monoxide.

FIG. 2.

Showing the value of the lower limit for carbon disulphide–air when part of the air is replaced by a third substance.



The present results are in general agreement with former work, and indicate that the addition of a small quantity of a large variety of substances raises the value of the lower limit for carbon disulphide–air. The large difference formerly noted between the behaviour of gases and that of certain vapours is now seen to have been due in part to the choice of gases, and in part to the small quantities of these that were used. The added substances appear

Table I.

Original temperature of mixtures, 15° ± 3°.

Combustible mixture.			Limit	Error
H_2.	CS_2.	Both.	(calc.).	%.
—	2·01	2·01		
0·30	2·08	2·38		
0·70	2·18	2·88		
1·31	2·32	3·63		
1·90	2·43	4·33		
2·44	2·45	4·89	5·54	+13
4·10	2·05	6·15	6·35	+ 3
5·15	1·71	6·86	6·86	0
5·81	1·45	7·26	7·20	− 1
7·49	0·74	8·23	8·09	− 2
9·0	—	9·0		
CO.	CS_2.	Both.		
—	2·00	2·00		
0·95	2·02	2·97		
2·00	2·05	4·05		
4·00	2·11	6·11		
5·60	2·17	7·77	8·6	+11
7·90	2·12	10·0	9·7	− 3
9·1	1·80	10·9	10·6	− 3
10·4	1·33	11·7	11·8	+ 1
11·8	1·00	12·8	12·8	0
13·8	0·50	14·3	14·2	− 1
15·7	—	15·7		
C_2H_4.	CS_2.	Both.		
—	2·01	2·01		
0·04	2·36	2·40		
0·07	2·58	2·65		
0·16	2·92	3·08		
0·25	3·04	3·29		
0·32	3·00	3·32		
0·43	2·99	3·42	3·92	+15
0·96	2·70	3·66	3·83	+ 4
1·54	2·16	3·70	3·74	+ 1
2·23	1·38	3·61	3·62	0
2·72	0·80	3·52	3·54	+ 1
3·42	—	3·42		
EtOH.	CS_2.	Both.		
—	2·01	2·01		
0·06	2·42	2·48		
0·09	2·63	2·72		
0·10	2·65	2·75		
0·14	2·87	3·01		
0·25	3·09	3·34		
0·33	3·08	3·41		
0·46	3·08	3·54	3·99	+13
0·87	2·91	3·78	3·98	+ 5
1·58	2·36	3·94	3·96	+ 1
2·38	1·59	3·97	3·94	− 1
3·90	—	3·90		

Combustible mixture.			Limit	Error
H_2.	CS_2.	Both.	(calc.).	%.
(Upper limit.)				
—	34·0	34·0		
3·18	28·6	31·8		
8·3	24·9	33·2		
18·8	18·8	37·6	20·7	−45
33·8	11·2	45·0	32·3	−28
46·4	5·1	51·5	48·8	− 5
74·0	—	74·0		
CH_4.	CS_2.	Both.		
—	2·00	2·00		
0·31	2·43	2·74		
0·65	2·77	3·42		
0·80	2·88	3·68		
0·94	2·94	3·88		
1·21	2·88	4·09	4·45	+ 9
1·58	2·75	4·33	4·58	+ 6
2·40	2·40	4·80	4·84	+ 1
3·08	2·02	5·10	5·05	− 1
4·75	1·02	5·77	5·59	− 3
6·12	—	6·12		
C_2H_2.	CS_2.	Both.		
—	2·01	2·01		
0·08	2·50	2·58		
0·23	2·84	3·07		
0·29	2·83	3·12		
0·42	2·78	3·20		
0·53	2·74	3·27	3·74	+14
1·26	2·02	3·28	3·44	+ 5
1·60	1·60	3·20	3·29	+ 3
2·23	0·74	2·97	3·03	+ 2
2·80	—	2·80		
H_2S.	CS_2.	Both.		
—	2·00	2·00		
0·11	2·22	2·33		
0·28	2·40	2·68		
0·56	2·51	3·07		
0·84	2·52	3·36	4·37	+30
1·22	2·43	3·65	4·51	+24
2·07	2·08	4·15	4·82	+16
2·69	1·79	4·48	5·02	+12
4·27	1·00	5·27	5·51	+ 5
6·05	—	6·05		
n-C_5H_{12}.	CS_2.	Both.		
—	2·01	2·01		
0·013	2·31	2·32		
0·05	2·81	2·86		
0·08	2·95	3·03		
0·13	3·05	3·18		
0·23	2·96	3·19	3·57	+13
0·46	2·67	3·13	3·20	+ 2
0·71	2·18	2·89	2·83	− 2
1·08	1·15	2·23	2·20	− 1
1·34	0·44	1·78	1·77	− 1
1·49	—	1·49		

TABLE II.

Original temperature of mixtures, 16° ± 3°.

N_2.	CS_2.	CO_2.	CS_2.	SO_2.	CS_2.	C_2N_2.	CS_2.	CCl_4.	CS_2.
—	2·01	—	2·01	—	2·01	—	2·01	—	2·01
3·8	2·07	4·0	2·15	1·8	2·09	1·9	2·11	0·75	2·12
7·6	2·13	6·0	2·22	5·5	2·28	3·0	2·16	1·6	2·24
14·2	2·23	8·0	2·28	10·0	2·52	3·7	2·21		
23·3	2·35	12·0	2·38	15·0	2·78				
40·9	2·63	20·0	2·60	20·0	3·08				

to function in three ways: (1) They alter the thermal constants of the mixture; (2) they alter the percentage of oxygen in the mixture; (3) they produce what may be termed a specific catalytic effect.

(1) The alteration of thermal constants would affect any mixture of air with a combustible, and is chiefly responsible for such phenomena as the greater extinguishing effect of carbon dioxide as compared with nitrogen.

(2) A small change in the oxygen content of a mixture usually causes only a small change in the lower limit except when the combustible : oxygen ratio is large, as when ammonia burns in air, or when much inert gas is used with a normal combustible. In the case of carbon disulphide (and, to a less extent, of hydrogen sulphide), however, this effect persists even when a large proportion of oxygen is present, as is seen from Table III. The difference between these substances and methane is illustrated in Fig. 3.

TABLE III.

Original temperature of mixture, 16° ± 3°.

% O_2 in mixture.	% CS_2 in lower-limit mixture.	% O_2 in mixture.	% H_2S in lower-limit mixture.
11·8	2·63	15·6	6·60
15·5	2·35	17·6	6·25
17·4	2·23	19·7	6·05
19·7	2·07	28·0	5·56
20·6	2·00	35·4	5·30
37·0	1·59	51·0	5·04
53·2	1·40	66·6	4·93
93·0	1·24		

Table IV shows that ether–carbon disulphide mixtures are similarly affected when 19·7% of oxygen is added. Here the magnitude

TABLE IV.

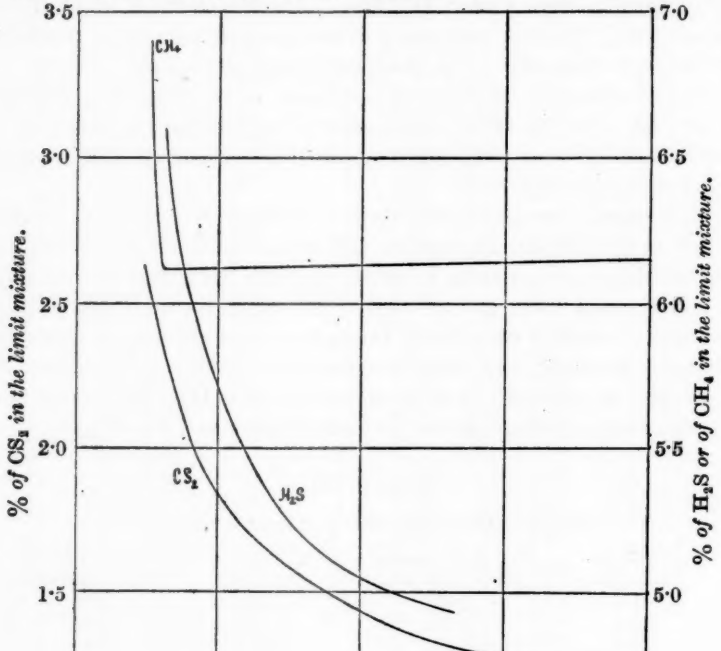
Original temperature of mixture, 15° ± 2°.

% CS_2 in combustible	100	98·5	95·0	85·0	75·0	50·0
% Ether in combustible	—	1·5	5·0	15·0	25·0	50·0
Limit in air	2·00	2·79	3·23	3·30	3·10	2·58
Limit when mixture contained 19·7% of added oxygen	1·61	2·36	2·88	2·98	2·84	2·42

of the effect decreases with decreasing proportion of disulphide, but it is still noticeable when the amount of ether is sufficient to inhibit the specific catalytic effect observed when small quantities of combustible vapours are added to carbon disulphide–air mixtures. This agrees with the fact that the addition of small quantities of several combustible substances to hydrogen sulphide–air was found to reduce

FIG. 3.

Showing the effect of varying oxygen content on the value of the lower limit for carbon disulphide, hydrogen sulphide, and methane.



the amount of hydrogen sulphide needed to give a limit mixture. This effect of oxygen content on the lower limit appears to be a property conferred by sulphur on certain of its compounds, but does not appear to be intimately connected with the catalytic effect originally observed.

Except when oxygen is added, any change in the oxygen content of a mixture depends only on the volume of the material added, so that, volume for volume, all substances should produce equal effects

from this cause. An upper limit to its value can be obtained from the results given by the addition of nitrogen, since the thermal constants of the mixture are hardly affected thereby. This effect is relatively small, and for most combustibles the rise in the lower limit is far greater than could be attributed to it, even when coupled with any change in the thermal constants of the mixture.

(3) The catalytic effect is the most important and varies tremendously from one substance to another. A comparison of the nitrogen figures with those for carbon monoxide and for cyanogen indicates that in both these cases the residual effect must be small, but for such substances as pentane and ethylene it is overwhelmingly great. This specific catalytic effect seems to be most pronounced for combustibles, although the difference found between carbon dioxide and sulphur dioxide indicates that the effect of the latter substance is greater than would be expected if due to its thermal properties alone. Carbon monoxide and cyanogen, which contain no hydrogen, behave almost as incombustibles; but the effect does not appear to be proportional to the amount of hydrogen in a compound, as may be seen by comparing the amounts of various substances needed to produce the same effect when small quantities are used. The order of efficacy of certain of those tested appears to be : Pentane and ethyl ether, acetaldehyde, ethylene, ethyl alcohol, acetylene, benzene, acetone, hydrogen sulphide, acetic acid, methane, hydrogen, cyanogen, carbon monoxide. This order suggests that ease of oxidation might prove to be an important factor. The relative positions of hydrogen and hydrogen sulphide also seem to point to the molecular nature of the effect, but the high thermal conductivity of hydrogen may be partly responsible for the small effect produced by this gas. Experiments with acetone and hydrogen showed that when used together they produced the effect to be expected from their behaviour when used separately.

Table I shows that as small quantities of the air in a carbon disulphide–air mixture are progressively replaced by a second combustible, the increase in the amount of the disulphide needed to give a lower-limit mixture becomes smaller, until the amount of disulphide present ultimately reaches a maximum and then diminishes. The maximum is attained more quickly the greater the original effect of the second combustible. The calorific value of the limit mixture containing most carbon disulphide is generally 900—950 Cals., but for hydrogen, hydrogen sulphide, and acetylene the value found is considerably below this. These gases give lower-limit calorific values well below the normal 1100—1200 Cals. when used with air alone, so that the fall in the amount of carbon disulphide in the mixture probably sets in when the second combustible

present begins to burn normally. After the amount of disulphide present has begun to diminish, the amounts of the two combustibles can be calculated approximately from Le Chatelier's rule, provided the value of the carbon disulphide lower limit be taken as 4·0%, and agreement with the rule generally becomes closer as the amount of disulphide diminishes. There is a similar tendency shown at the upper limit, but here it is not so well defined. At the lower limit, Le Chatelier's rule is followed fairly well over two-thirds or more of the range of mixtures, as measured by the amount of the second combustible present. In the presence of a minimum quantity of some other combustible, carbon disulphide behaves as though its calorific value at the lower limit was 1060 Cals., a value not very different from that normally found for vapours (J., 1922, **121**, 1244). It is important that this occurs even with carbon monoxide, which has such a very small effect in raising the value of the lower limit of the disulphide. When burning alone, carbon disulphide–air can propagate flame if the calorific value of the mixture exceeds 530 Cals. Carbon disulphide thus appears to possess two different modes of combustion, and there is no reason to doubt the explanation formerly advanced to explain the results then available, *viz.*, that the ordinary limit combustion of carbon disulphide is catalysed, probably by some product of its combustion, and that this catalysis is hindered by a large variety of substances. Of the gases known to be produced when the disulphide burns, the only one found to reduce the value of the limit was carbon oxysulphide, and this had an effect considerably less than that produced by an equal volume of the disulphide. The oxysulphide and oxygen were the only two substances tested which did not hinder the burning of carbon disulphide.

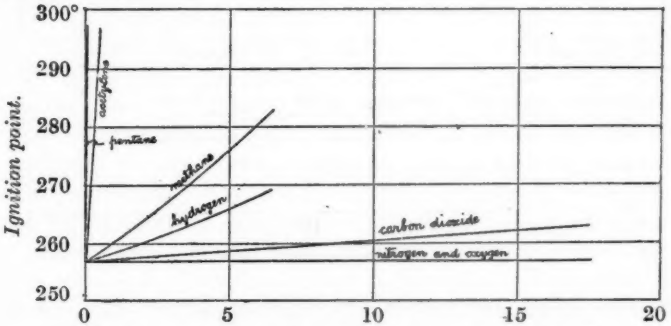
Dixon (*loc. cit.*) suggests that the product catalysing the ignition of carbon disulphide is the monosulphide of carbon. If this is the explanation of the limit results given by carbon disulphide, the phenomenon should be confined to substances containing both sulphur and carbon, such as the disulphide and oxysulphide of carbon. This idea is supported by the behaviour of hydrogen sulphide, which does not exhibit this phenomenon, whilst its lower limit is also calculable from the lower limit for hydrogen and the theoretical (calorific value) limit for sulphur. This might, however, be due to the large amount of hydrogen in the molecule.

To test the monosulphide theory it was decided to examine the effect of certain combustible substances on the ignition point of sulphur itself. To this end sulphur was heated in a glass tube 1·5 cm. in diameter. The temperature of the sulphur was taken by means of a thermometer immersed in it, whilst the necessary air for combustion

was introduced by means of a side tube at the surface of the sulphur. The procedure adopted was to introduce a slow stream of air (or air containing the substance under test) through the side tube, after which the stream of gas was gradually cut off. Ignition then took place if the sulphur was just above its ignition point. For comparison, relative values of the ignition temperature of mixtures of 3% carbon disulphide–air with a third substance were determined by evacuating glass bulbs of 12—15 c.c. capacity, and then allowing the appropriate mixture to flow into the bulb. As the figures obtained have no absolute significance, the results are only shown graphically (Figs. 4 and 5), but small quantities of hydrogen sulphide also raised the ignition point of sulphur materially. There is a

FIG. 4.

Showing the ignition point of sulphur when the air passed over it contains various substances.



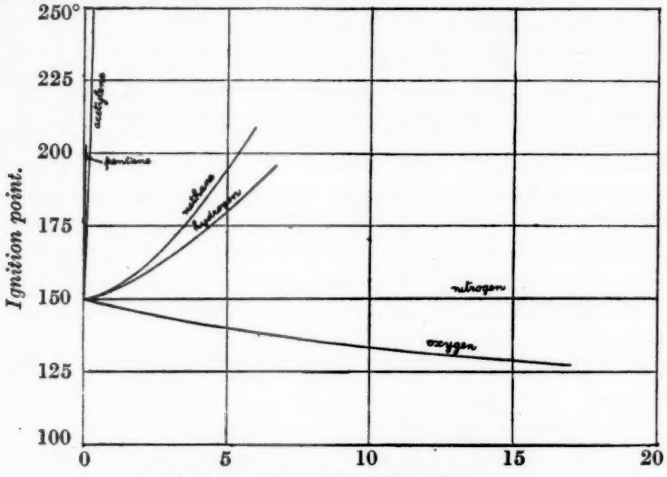
striking similarity between the general form of the two series of results, despite the greater magnitude of the rise produced in the case of carbon disulphide. The ignition of sulphur is materially hindered by small quantities of various substances, and is thus probably itself a catalysed phenomenon. The ignition and combustion of carbon disulphide may be catalysed by carbon monosulphide, but the occurrence of a somewhat similar phenomenon in the case of sulphur renders it extremely unlikely that the monosulphide is the sole catalysing agent.

Attention must be directed to certain differences between the results given by the present work and those found by Dixon. The order of efficacy of certain substances as gauged by their power of preventing the propagation of flame at the limit in carbon disulphide–air is given on p. 799. As regards their effect on the ignition of carbon disulphide, Dixon classes ethylene and acetylene as poisonous and pentane, carbon monoxide, methane, and ethyl ether as

noxious, whilst hydrogen is grouped with carbon dioxide and nitrogen as inert. Delépine's work (*loc. cit.*) is probably not so closely connected with the present communication, but it is noteworthy that acetic acid, which he found to promote the autoxidation

FIG. 5.

Showing the ignition point of a 3% carbon disulphide–air mixture when some of the air is replaced by a third substance.



of certain sulphur compounds, has a distinct hindering effect on the propagation of flame in carbon disulphide–air near the limit.

I desire to thank Messrs. Nobel Industries, Ltd., and particularly Mr. W. Rintoul, Manager of the Research Section, for facilities accorded me for carrying out this work.

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CXVII.—*The Velocity of Formation of Quaternary Ammonium Salts from Trimethylamine and Benzyl Chloride and the Three Mononitrobenzyl Chlorides.*

By HAMILTON MCCOMBIE, HAROLD ARCHIBALD SCARBOROUGH, and FREDERICK FRANCIS PERCIVAL SMITH.

IT has been shown (J., 1926, 2863) that the relative order of the velocity of saponification of the isomeric methoxybenzoic esters and of ethyl benzoate is not the same in the two alcohol–water

mixtures used as solvents. This behaviour appeared to be unusual and to require further investigation.

The choice of a suitable reaction which can be followed in a wide range of solvents is almost limited to the formation or decomposition of ammonium or sulphonium salts. The reaction selected was the formation of a quaternary ammonium salt from trimethylamine and a substituted benzyl chloride. The isomeric nitrobenzyl chlorides have been used by previous investigators and were deemed to be of interest for our present purpose.

Several workers have assumed that the effect of a substituent upon the velocity of reaction will depend upon the precise mechanism by which interaction takes place; this applies equally whether the effect be a general or an alternating effect. This assumption appears to be well illustrated by the behaviour of the alkyl and aryl halides with a number of reagents. It was pointed out by Slator (J., 1909, **95**, 100) that the results fell into at least two types when a comparison was made between the velocity coefficients of a series of reactions in which an organic halide was one of the reactants; thus the results with sodium ethoxide, sodium acetoacetate, and sodium thiosulphate showed great similarities. A second type of result was obtained with dissolved oxygen and with silver nitrate. The reaction with hydrolysing reagents gave results which differed in type from both the other classes. This division into types would appear to be true even when the comparison is drawn between three isomerides. The velocity coefficients for the reaction of the nitrobenzyl chlorides with a hydrolysing reagent (Olivier, *Rec. trav. chim.*, 1922, **41**, 646), with sodium thiosulphate (Slator, *loc. cit.*), and with potassium iodide (Conant, *J. Amer. Chem. Soc.*, 1925, **47**, 488) show this difference in type (Table I).

TABLE I.

Reagent.	Solvent.	Benzyl chloride.	Relative values of k. Nitrobenzyl chlorides. *ortho.*	*meta.*	*para.*
Alkali.	Aq. alcohol.	22·6	1·06	1·28	1·00
Sodium thiosulphate.	,,	0·54	0·54	0·64	1·00
Trimethylamine.	,,	—	0·81	0·86	1·00
Potassium iodide.	Acetone.	0·14	1·32	0·57	1·00
Trimethylamine.	,,	0·98	0·55	0·80	1·00

It is seen that on hydrolysis the benzyl chloride and the *m*-nitrobenzyl chloride have relatively higher velocity coefficients, whereas in the other reactions the *p*-nitrobenzyl chloride has the highest of these three. It would seem impossible to include the ortho-substituted halide in any generalisation, as the steric factor is variable and occasionally unexpected in its effects. A consider-

ation of the results recorded in Tables I and II may be divided into two parts: first, the general effect of the nitro-group on the reactivity of the chlorine in the benzyl chloride molecule, and, secondly, the relative reactivities of the *o*-, *m*-, and *p*-nitrobenzyl chlorides.

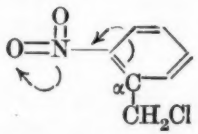
In connexion with the results obtained by Olivier (*loc. cit.*) for the hydrolysis of the nitrobenzyl chlorides, Robinson (J., 1926, 384) has suggested a mechanism based essentially upon the relative strengths of benzoic acid and the nitrobenzoic acids. Since the results obtained with potassium iodide, sodium thiosulphate, and trimethylamine differ so widely from those obtained on hydrolysis, it would appear that some other mechanism is involved.

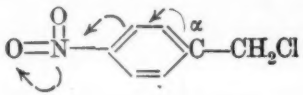
To explain these results, the authors base their suggestions upon the relative strengths of the nitrophenols or of the nitrobenzoic acids as compared with the unsubstituted compounds. Since the substituted compounds have higher dissociation constants than the corresponding unsubstituted compounds, the general effect of the nitro-group is to give the benzene ring, as a whole, a higher affinity for a negative charge; further, they suggest that this attraction of electrons towards the nitro-group may proceed so far that the negative electronic attraction between the hydrogen and oxygen atoms may be converted into a positive repulsion between the nuclear charges of these atoms. In the event of dissociation, it is assumed that the valency electrons would be retained by the heavier nuclear charge of the oxygen atom, and the hydrogen would be thus liberated as a positive ion. If this conception is extended to the nitrobenzyl chlorides, it is seen that the nitro-group causes a movement of electrons towards itself and, as a consequence, repulsion of the nuclear charge of the chlorine atom may occur; there is, however, one essential difference, since, if the chlorine breaks away, it would be expected to do so as a negative ion, and this would necessitate the valency electrons of the carbon–chlorine union going with the chlorine atom. Thus the carbon–chlorine union in the nitrobenzyl chlorides is under a greater strain than that in the unsubstituted benzyl chloride, but this strain may be opposed by a second influence, since, if the chlorine is dissociated, the benzyl residue would become a positive ion which would be inconsistent with its greater affinity for a negative charge.

In the reactions with sodium thiosulphate and with potassium iodide, the product of the reaction is of a similar chemical nature to one of the reactants, and since no positive ion is formed by the benzyl residue, the difference in the velocity coefficients of the substituted and of the unsubstituted benzyl chlorides is to be ascribed to the strain on the carbon–chlorine union caused by the

nitro-group. The reaction with trimethylamine is a special case, since in this reaction the chlorine is detached as a negative ion and the benzyl residue becomes part of the positive benzyltrimethylammonium ion, and the strain upon the carbon–chlorine union may be partly or completely neutralised by the resistance of the substituted benzyl residue to forming a part of this positive ion.

In a consideration of the alternating effect of the nitro-group, Robinson has shown (*loc. cit.*) that an electronic drift is caused in the direction of this grouping which may be represented as follows:





and that this drift will be most marked in the case of the *o*- and *p*-isomerides. Its effect will be to leave the carbon atoms marked α more positive than they were before the introduction of the nitro-group, and consequently the alternate effect will be in the same direction as the general effect.

In applying these considerations to groups other than the nitro-group, it was noted that, if the suggested electronic drifts of the general and of the alternate effects were in the same direction (*e.g.*, with the NH_2 and CH_3 groups), then

$$k_m > \text{or} < k_p \text{ according as } k_{\text{unsubs.}} > \text{or} < k_{\text{subs.}}.$$

In the case of the methoxy-group, the general effect is small and no generalisation is possible, and in the case of the halogens, the general and alternate effects are opposed.

Various views have been put forward to explain solvent effect; thus Cox (J., 1921, **119**, 142) suggested the formation of solvent–solute complexes, but Hawkins (J., 1922, **121**, 1170) was unable to obtain any evidence that such compounds exist. The effect due to the viscosity of the solvent has been examined by Buchböck (*Z. physikal. Chem.*, 1900, **34**, 229).

Arrhenius (*ibid.*, 1889, **4**, 226) was the first to suggest that molecules must be activated before they can enter into reaction. This energy of activation has more recently been ascribed to radiation (Lewis, J., 1914, *et seq.*) and to molecular collisions between the reacting molecules (Hinshelwood, *Phil. Mag.*, 1926, **2**, 360). The authors suggest that in the case of a reaction taking place in solution, the solvent itself activates the reacting molecules by means of its external electrical field. It is impossible to obtain a measure of this, as it is not completely expressed by the dielectric constant, by the chemical reactivity, or by the solvent power. It

TABLE II.

(*p*-Nitrobenzyl chloride, $k = 1$.)

Solvent.	Benzyl chloride.	Nitrobenzyl chlorides. *ortho.*	*meta.*
Ethyl acetate	0·62	0·42	0·79
Acetone	0·97	0·55	0·80
Benzene	1·02	0·68	0·74
Ethyl benzoate	1·08	0·63	0·72
Anisole	1·32	0·70	0·71
Nitrobenzene	1·45	0·67	0·68
Ethyl alcohol	—	0·69	0·87
94·45% Alcohol–Water	—	0·69	0·85
Acetonitrile	—	0·79	0·87

might be expected that the presence of such groupings as an ethylenic linking, or of such elements as nitrogen, oxygen, or the halogens in a solvent would tend to increase the power of the solvent as an activating agent. The results recorded in Table II are in accord with these views. That the polarising action of the solvent is not its only effect, however, is shown in Table III, in which the columns headed 1, 2, 3, and 4 give respectively the relative reaction coefficients for the addition of trimethylamine to *p*-nitrobenzyl chloride, of ethyl iodide to triethylamine, of aniline to bromoacetophenone, and of allyl bromide to pyridine.

TABLE III.

Solvent.	1.	2.	3.	4.
Hexane	1	0·46	—	—
Ether	1·8	—	14	—
Benzene	17	17	17	17
Ethyl alcohol	108	94	680	136
Benzyl alcohol	298	332	510	—
Methyl alcohol	298	130	1020	—
Acetone	497	149	340	289
Nitrobenzene	1060	—	170	731
Acetophenone	890	—	—	595

Further consideration of the results given in Table II shows that the first six solvents stand in the order in which they decrease the value of the ratios k_m/k_p, k_p/k_o, and of $k_{\text{subs.}}/k_{\text{unsubs.}}$. These regularities are capable of explanation if it is assumed that the solvent has the power to increase or decrease the effect of the nitro-group on the halogen atom. In the ratios k_m/k_p and k_p/k_o, which depend upon the alternating effect of the nitro-group, the solvents in the given order increase the electronic drift, and since this is more powerful in the *p*- than in the *m*-position, the ratio k_m/k_p decreases.

The given range of solvents appears to influence the general effect in exactly the opposite order. Thus a range of solvents

increasing the velocity of interaction of the *p*-nitrobenzyl chloride relatively to the *m*-isomeride should increase $k_{\text{subs.}}$ relatively to $k_{\text{unsubs.}}$, whereas the ratio decreases. Alcohol, acetonitrile, and anisole show yet a third effect of the solvent in that the ratios k_m/k_p and k_o/k_p are increased by these three solvents.

Dimroth (*Annalen*, 1910, **377**, 131) showed that the effect of solubility of the reactant in an intramolecular change was represented by $k \propto 1/S$, where k is the velocity coefficient and S the solubility of the starting product. It was shown that in the reaction between trimethylamine and *p*-nitrobenzyl chloride the relationship $k \propto 1/S_1S_2$ was not true (von Halban, *loc. cit.*). It appeared of interest to test the formula for the *meta*/*para* and *ortho*/*para* ratios of the nitrobenzyl chlorides. The relationship becomes $(k_m/k_p)(S_m/S_p) = \text{const.}$, since the solubility of the amine cancels out. It will be seen from Table IV that, even when the solubility ratios vary over a range of 50% and the velocity ratios over a similar range, no constant could be obtained.

TABLE IV.

	m/*p* Ratios.			*o*/*p* Ratios.		
Solvent.	100 k_m/k_p.	S_m/S_p.	Product.	100 k_o/k_p.	S_o/S_p.	Product.
Benzene	74	—	—	66·1	4·09	270
Ethyl acetate	78·7	5·65	490	41·8	3·69	154
Acetone	80·1	5·08	410	55·5	3·41	189
Ethyl benzoate	72·4	5·19	375	63·2	3·34	211
Nitrobenzene	68	4·78	325	67	3·18	212
Alcohol	86·6	3·79	320	69·5	3·20	222

EXPERIMENTAL.

The *o*- and *m*-nitrobenzyl chlorides were Kahlbaum products; the *p*-nitrobenzyl chloride was prepared by the nitration of benzyl chloride according to the method of Beilstein (*Annalen*, 1866, **139**, 337). The solvents acetone, acetonitrile, and anisole were B.D.H. products; the ethyl acetate, ethyl benzoate, and nitrobenzene were prepared in the usual manner. The trimethylamine was stored as the hydrochloride, from which the free amine was liberated, as required, by warming with concentrated aqueous potassium hydroxide. The gas was dried by passing through a series of soda-lime tubes, and absorbed immediately in the freshly-distilled solvent. The solution was standardised by titration against hydrochloric acid, a mixture of methyl-orange and sodium indigotin-sulphonate being used as indicator.

The reaction was carried out in sealed tubes, each containing 10 c.c. of the amine and 10 c.c. of the chloride solution. The tubes

were filled, drained, and sealed whilst immersed in an ice-bath. Zero time was assumed to be the moment at which the tubes were placed in the thermostat, which was at 30° ± 0·1°. Usually seven tubes were used for each determination.

The ionisable chlorine was estimated gravimetrically. The tube was smashed under alcoholic silver nitrate and the solution diluted with water. This procedure ensured that all the quaternary ammonium chloride reacted with the silver nitrate, as it was found that with such solvents as nitrobenzene a mere shaking with aqueous silver nitrate was insufficient for a quantitative extraction. A slight modification was necessary in the experiments in which benzyl chloride was used: the tube was opened under water and the mixture shaken with benzene to remove unchanged benzyl chloride; the benzene was washed with small volumes of water, the wash-waters were added to the aqueous layer, and excess of silver nitrate was added. The silver chloride precipitates were weighed in a series of Gooch crucibles.

The solubilities of the nitrobenzyl chlorides (Table VIII) were determined by weighing solvent and solute into small bulbs, sealing off, and heating with shaking until solution was complete. The first reading was usually rejected; the succeeding three or four agreed within 0·1°, and this temperature was accepted as that of solution. Five determinations, with varying weights of solvent, were used in constructing a curve from which the solubility at 30° could be read off.

In the Tables V—VII, a represents the concentration of amine and b that of the benzyl or nitrobenzyl chloride expressed in g.-mol./litre.

TABLE V.

Benzyl chloride and trimethylamine in acetone.

$a = 0·1362$; $b = 0·1101$.

Time (mins.).	Wt. of AgCl.	x.	$k \times 10^4$.
73	0·1350	0·0471	698
90	0·1514	0·0528	691
135	0·1873	0·0653	695
178	0·2077	0·0725	692
210	0·2221	0·0775	685
244	0·2330	0·0813	685
310	0·2548	0·0889	702
		Mean	692

TABLE VI.

m-Nitrobenzyl chloride and trimethylamine in acetonitrile.

$a = 0·09377$; $b = 0·04490$.

Time (mins.).	Wt. of AgCl.	x.	$k \times 10^3$.
63	0·0670	0·0234	146
70	0·0717	0·0250	146
80	0·0765	0·0267	145
100	0·0844	0·0294	142
113	0·0887	0·0310	141
124	0·0927	0·0324	142
		Mean	143

It was found that the quaternary ammonium salts were almost insoluble in benzene, ethyl acetate, and ethyl benzoate, slightly soluble in acetone, and easily soluble in nitrobenzene.

TABLE VII.

Benzyl chloride and trimethylamine.

Solvent.	*a*.	*b*.	Limit *k*.	Mean *k*.
Ethyl acetate ...	0·1647	0·1994	0·00650—0·00705	0·0067
Acetone	0·1362	0·1101	0·0680 —0·0700	0·069
Benzene	0·3006	0·3465	0·00247—0·00250	0·00248
Ethyl benzoate ...	0·2165	0·1497	0·0237 —0·0254	0·0238
Anisole	0·1894	0·2012	0·0205 —0·0217	0·0212
Nitrobenzene	0·0836	0·0492	0·211 —0·221	0·218

o-Nitrobenzyl chloride and trimethylamine.

Ethyl acetate ...	0·1392	0·1699	0·00440—0·0046	0·00452
Acetone	0·0651	0·0730	0·0388 —0·0398	0·0394
Benzene	0·1855	0·1642	0·00155—0·00163	0·00160
Ethyl benzoate ...	0·0855	0·1248	0·0133 —0·0147	0·0139
Anisole	0·2365	0·1712	0·0111 —0·0113	0·0112
Nitrobenzene	0·1153	0·0711	0·0995 —0·103	0·101
Ethyl alcohol ...	0·1552	0·0835	0·0118 —0·0124	0·0122
94·45% Alcohol	0·1330	0·0726	0·0142 —0·0149	0·0145
Acetonitrile	0·1357	0·0771	0·129 —0·132	0·130

m-Nitrobenzyl chloride and trimethylamine.

Ethyl acetate ...	0·1572	0·1339	0·0083 —0·0087	0·0085
Acetone	0·1334	0·0635	0·0541 —0·0578	0·0568
Benzene	0·1828	0·1538	0·00167—0·00190	0·0018
Ethyl benzoate ...	0·1961	0·1344	0·0155 —0·0164	0·0160
Anisole	0·2393	0·1904	0·0111 —0·0119	0·0114
Nitrobenzene	0·1182	0·0722	0·098 —0·103	0·102
Ethyl alcohol ...	0·1798	0·0909	0·0148 —0·0157	0·0151
94·45% Alcohol	0·1330	0·0722	0·0177 —0·0184	0·0179
Acetonitrile	0·0938	0·0449	0·141 —0·146	0·143

p-Nitrobenzyl chloride and trimethylamine.

Ethyl acetate ...	0·1572	0·1413	0·0104 —0·0113	0·0108
Acetone	0·1365	0·0627	0·0698 —0·0729	0·071
Benzene	0·1784	0·1604	0·00236—0·00250	0·0024
Ethyl benzoate ...	0·2062	0·1353	0·0214 —0·0227	0·0221
Anisole	0·2369	0·1847	0·0156 —0·0168	0·0160
Nitrobenzene	0·1167	0·0631	0·145 —0·157	0·150
Ethyl alcohol ...	0·1801	0·0881	0·0170 —0·0179	0·0175
94·45% Alcohol	0·1330	0·0695	0·0209 —0·0213	0·0210
Acetonitrile	0·0795	0·0437	0·158 —0·172	0·175

TABLE VIII.

Solubilities of the nitrobenzyl chlorides at 30°.

(G. of chloride per 100 g. of solvent.)

Solvent.	*ortho*-.	*meta*-.	*para*-.
Acetone	433	644	126·8
Benzene	304	—	74·2
Ethyl acetate	257	394	69·7
Nitrobenzene	217	326	68·2
Ethyl benzoate	171·3	266	51·2
Ethyl alcohol	26·3	30·4	8·2

One of the authors (F. F. P. S.) expresses his thanks to the Department of Scientific and Industrial Research for a grant which has enabled him to collaborate in this work.

THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE. [*Received, December 31st*, 1926.]

CXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XIII. The Nitration of Some γ-Phenylpropylamine Derivatives.*

By CHRISTOPHER KELK INGOLD and IAN STUART WILSON.

FOR reasons which will be apparent from the introductory statement of Part X (this vol., p. 250), we have studied the nitration of γ-phenylpropylammonium nitrate and of γ-phenylpropyltrimethylammonium picrate. The proportions of *m*-isomeride formed are given in the lowest line of the following table, the other numerical values being taken from previous papers (*loc. cit.*, and J., 1926, 2441) to illustrate the effect of homology.

Nitration in Nitric Acid at 0° to − 15°.

	$C_6H_5\cdot[CH_2]_x\cdot NH_2HX$ (primary).	$C_6H_5\cdot[CH_2]_x\cdot NMe_3\}X$ (quaternary).
$x = 1$	49%	88%
$x = 2$	12%	19%
$x = 3$	3%	5±2%

[The limits attached to the figure for the last quaternary salt arise from the circumstance that the proportion of nitrated salt which cannot be separated from the inorganic salts produced on neutralising the nitration solution is of the order of magnitude of the quantity of *m*-derivative formed; therefore, the unknown quantity of *m*-compound which may be contained in this unseparated portion cannot be neglected in comparison.]

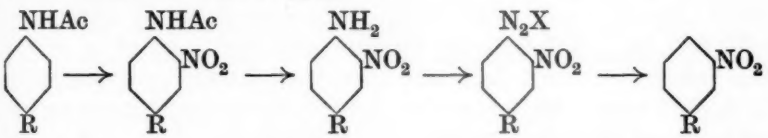
EXPERIMENTAL.

γ-Phenylpropyltrimethylammonium Picrate.—γ-Phenylpropylamine was prepared by Michaelis and Jacobi's method (*Ber.*, 1893, **26**, 2160) and purified by conversion into the oxalate. This salt (10 g.) was boiled for a few minutes with ethyl alcohol (380 c.c.) and anhydrous sodium carbonate (38 g.), and the cooled mixture treated with 41 c.c. of methyl sulphate. The reaction was completed by boiling for 2 hours, and after the addition of water the excess of methyl sulphate was destroyed and the greater portion of the alcohol was removed by distillation. The aqueous solution (250 c.c.)

was extracted twice with ether to remove tertiary bases, and, after expulsion of the dissolved ether by boiling, was mixed with a saturated solution of sodium picrate. The salt which separated crystallised from aqueous alcohol in orange-yellow prisms, m. p. 121° (Found: C, 53·2; H, 5·6. $C_{18}H_{22}O_7N_4$ requires C, 53·2; H, 5·5%).

γ-p-*Nitrophenylpropyltrimethylammonium picrate* was prepared from γ-*p*-nitrophenylpropylamine (below) by the same method (Found: C, 47·7; H, 4·8. $C_{18}H_{21}O_9N_5$ requires C, 47·9; H, 4·7%). It forms yellow prisms, m. p. 138°.

γ-m-*Nitrophenylpropyltrimethylammonium Picrate.*—This was synthesised, by the following process, from the *p*-isomeride, which was first converted into the corresponding *p*-acetamido-compound [R = $\cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot \overset{+}{N}(CH_3)_3$]:



A solution of the *p*-nitro-picrate (10 g.) in concentrated hydrochloric acid (200 c.c.) was shaken with benzene to remove the picric acid and then reduced with stannous chloride (25 g.) at 100° during 0·75 hour. After dilution, the tin was removed as sulphide and the solution evaporated to dryness. The *dihydrochloride* thus obtained was acetylated by boiling with acetic anhydride (20 c.c.) and anhydrous sodium acetate. The residue obtained on evaporation to dryness was dissolved in water and the solution mixed with saturated sodium picrate solution. Very little picrate was precipitated by this means, and the solution was therefore evaporated to dryness and the residue extracted with acetone. The salt dissolved by the acetone was crystallised first from water and then from alcohol (m. p. 153°; yield 50%). The γ-p-*acetamidophenylpropyltrimethylammonium picrate* so obtained was nitrated at − 18° during 2 hours with 7·5 parts of nitric acid (*d* 1·49). The solution was allowed to warm to 0° during 15 minutes, mixed with two volumes of ice (picric acid was precipitated), and neutralised with concentrated sodium hydroxide solution (picric acid redissolved and a picrate crystallised). γ-m-*Nitro*-p-*acetamidophenylpropyltrimethylammonium picrate* separates from alcohol in prisms, m. p. 140° (Found: C, 47·9; H, 5·0. $C_{20}H_{24}O_{10}N_6$ requires C, 47·3; H, 4·8%). It was boiled gently with ethyl alcohol (40 parts) and concentrated sulphuric acid (4 parts) until the volume was reduced to one-third; a further quantity of alcohol was then added and the boiling continued until ethyl acetate ceased to be contained

in the distillate. The solution was diluted with fresh alcohol, neutralised with anhydrous sodium carbonate, and filtered, and the residue was well washed with alcohol. The combined filtrates were evaporated to a small bulk, acidified with concentrated sulphuric acid, and diazotised at 0° with a saturated solution of sodium nitrite. The solution was then heated at 100° until nitrogen ceased to be evolved, treated with excess of anhydrous sodium carbonate and sodium picrate, and evaporated to dryness. The residue was extracted with boiling acetone, and the residue obtained on evaporating the acetone was re-extracted with hot ethyl acetate, from which the m-*nitro-picrate* separated in yellow needles, m. p. 156° (Found: C, 48·2; H, 4·8. $C_{18}H_{21}O_9N_5$ requires C, 47·9; H, 4·7%). Its constitution was proved by oxidation (below).

Nitration of γ-Phenylpropyltrimethylammonium Picrate.—The picrate (5·00 g.) was added during 1 hour to 25 c.c. of nitric acid ($d^{10°}$ 1·49) at − 15°, and the mixture was then kept at or below this temperature for 1 hour and thereafter allowed to warm to 5° during 0·5 hour. Ice was added, and the solution rendered alkaline with concentrated sodium hydroxide solution at − 10°. The nitro-derivative was collected, and crystallised from methyl alcohol and ethyl acetate until no further crops of pure *p*-isomeride (total 47%) could be obtained. All the solutions were then evaporated to dryness and the residues extracted in a Soxhlet apparatus with acetone; the residues from the acetone were again extracted with ethyl acetate, the final product being washed with a very little water. The yield was 49%, making a total yield of mononitro-products equal to 96%. The mixture of isomerides (Found: C, 48·3, 48·4; H, 5·0, 4·9. Calc.: C, 47·9; H, 4·7%) was oxidised in 84% yield to nitrobenzoic acids by permanganate, and the *p*- and *m*-acids were estimated by separation as described in previous parts of this series (*p*-, 66%; *m*-, 6·5%).

Two parallel experiments in which the pure *p*- and *m*-nitro-picrates were separately oxidised to the corresponding nitrobenzoic acids by means of permanganate gave yields amounting to 81% and 80%, respectively. This shows that there is no selective destruction of the *m*-isomeride during the oxidation mentioned in the preceding paragraph, and that the proportion of *m*-nitrobenzoic acid represents the proportion of *m*-nitro-picrate in the mixture oxidised.

On this assumption, there is 3·2% of *m*-isomeride in the 96% of mononitration product accounted for. The total formed could not be more than 7·2%, and is very unlikely to be so much. The proportion of *p*-isomeride is $47 + 0{\cdot}49 \times 66 \pm 2 =$ about 81%.

Nitration of γ-Phenylpropylamine.—The base was run through a

capillary tube into 7·5 parts of nitric acid (*d* 1·49) at — 15°. Two hours were allowed for the nitration and the nitric acid solution was then warmed to 5° and mixed with ice.

γ-p-*Nitrophenylpropylammonium nitrate* (48·5%) was obtained in needles, m. p. 200°, from the crystalline mixture of nitrates by crystallisation from water. The corresponding *chloride* forms prisms, m. p. 165° (Found : C, 50·2; H, 6·2. $C_9H_{13}O_2N_2Cl$ requires C, 49·9; H, 6·0%). Small amounts of neutral and acid oxidation products were removed from the combined liquors by extraction with ether, and the remainder of the mononitration product (40%) was then isolated by basifying it with sodium hydroxide and again extracting it (Found for the corresponding nitrates : C, 45·0; H, 5·1. Calc. : C, 44·4; H, 5·4%). This was oxidised in 66% yield to a mixture of nitrobenzoic acids, the *p*- and *m*-acids in which were estimated by separation as before (*p*-, 55%; *m*-, 6%). The pure *p*-acid, on oxidation under the same conditions, gave *p*-nitrobenzoic acid in 67% yield.

The proportions of *m*- and *p*-isomerides calculated on the total mononitration product are therefore *m*-, 2·7%; *p*-, 73%.

The authors desire to thank the Royal Society for a grant which has covered part of the cost of this work.

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CXIX.—*The Nature of the Alternating Effect in Carbon Chains. Part XIV. The Directive Action of Groups of the Form* $-CH_2{\cdot}SO_2{\cdot}R$ *in Aromatic Substitution.*

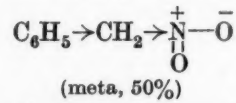
By CHRISTOPHER KELK INGOLD, EDITH HILDA INGOLD, and FLORENCE RUTH SHAW.

THE characteristic actions of a pole and of a dipole in controlling the position of substitution of a benzene derivative having been established in broad outlines by recent investigations (see below), a number of subsidiary influences required elucidation. The following will be considered.

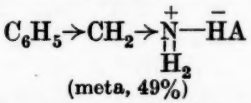
(i) *Influence of neutral* * *atoms in modifying the orienting effect of a charged atom.* The nitro-group contains a neutral as well as a negative oxygen atom, and when comparing the electron-

* Here, as previously, the term "neutral" is used relatively and is not intended to exclude atoms carrying the feeble charges represented by $\delta+$ and $\delta-$.

affinities of the nitro- and ammonium salt groups, as measured by their meta-directive effects in the nitration of phenylnitromethanes and benzylamine salts, Baker and Ingold (J., 1926, 2462; this vol., p. 261) assumed that the influence of the neutral

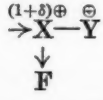


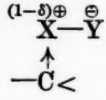
(meta, 50%)



(meta, 49%)

atoms attached to the positive ends of the dipoles would be small in comparison with the effect of the dipoles themselves. This is doubtless correct in the cases considered, but it is nevertheless conceivable that atoms of greatly differing electron-affinities (*e.g.*, carbon and fluorine) might allow their electrons to be attracted by a charged atom in such different degrees as to modify the effective charge on that atom, if not largely, at least to an appreciable extent:

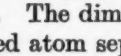




This effect has been searched for and has now been detected.

(ii) *Influence of a second charged atom: Compensation by the more distant end of a dipole.* The smaller *m*-directive action observed in phenylnitromethanes and benzylamine salts of the above types, as compared with the benzyltrialkylammonium ion (meta, 85—88%) (Goss, Ingold, and Wilson, J., 1926, 2440; Goss, Hanhart, and Ingold, this vol., p. 250), has been attributed (J., 1926, 2445) to partial compensation by electron-repulsion from the more distant negative end of the dipole. In the above examples, however, the negative charges are carried by different kinds of atoms, and for a strict demonstration of this principle it is desirable (see below) that atoms of the same kind should be used, and only the total charges varied. This method is employed in the present work, and the effect of varying the compensating charge in the ratio 3/2 is recorded.

(iii) *Damping action of external electron-shells in positively charged atoms.* The diminution in the *m*-directive influence of a positively charged atom separated from the nucleus by an increasing number of neutral atoms (Part X, *loc. cit.*) shows that each group of electrons through which the electron-strain is transmitted exerts an appreciable damping action:



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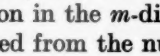
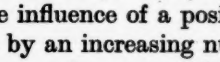


88%



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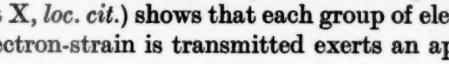


5±2% of *m*-nitro-derivative.

Since the positive electricity with which the strain originates resides at the *nucleus* of the charged atom, a similar damping action may be expected to arise during the passage of the effect through the successive shells of electrons belonging to the charged atom itself, and this consideration enables us to forecast the relative orienting influences of equivalent ionic charges carried by different atoms. Phosphorus and sulphur atoms in the combined state possess a group of eight electrons external to the ten which correspond with the ten in the combined nitrogen atom; arsenic, selenium, and iodine atoms contain groups additional to those present in phosphorus and sulphur. It follows that phenyl- and benzyl-phosphonium and -thionium ions should exhibit weaker *m*-directive action than the analogous phenyl- and benzyl-ammonium ions; that phenyl and benzyl sulphoxides (dipole) should show weaker *m*-orientation than the corresponding aromatic nitro-compounds; that aromatic arsonium and selenonium salts should show weaker *m*-reactivity than the comparable phosphonium and thionium salts, and so forth.* Of course, apart from this screening action of the outer electrons, the magnitude of the effect escaping from a charged atom will depend on the ionic charge; whence it follows, also, that aromatic sulphones (double dipole) should show stronger *m*-orienting action than the corresponding sulphoxides (unit dipole). The testing of such predictions as these is necessarily a lengthy task, but we are already able to advance evidence showing that the nitrogen and sulphur atoms stand in the anticipated order.

Results.

In the experimental section a comparative study is recorded of the nitration of a series of benzylsulphonyl compounds of the general formula $C_6H_5\cdot CH_2\cdot SO_2\cdot R$. The results, so far as they bear upon the three topics raised, may be summarised as follows:

Nitration of Benzylsulphonyl Compounds, $C_6H_5\cdot CH_2\cdot SO_2\cdot R$ *in Nitric Acid* ($d^{18°}$ 1·494) *at* $-10°$ *to* $-5°$.

Group R	CH_3	NH_2				OH	Cl
Meta (%)	30	31				14	51
Group R		NHMe	NHEt	NMe_2	NEt_2	OMe	
Meta (%)		29	28	28	25	32	

Although based for the most part on tolerably consistent triplicate determinations (for details, see Table, p. 832), these figures can

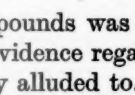
* The same principles, applied to the fractional dipoles discussed in the following paper, show that $C_6H_5\cdot SiCl_3$ and $C_6H_5\cdot CH_2\cdot SiCl_3$ should exhibit weaker *m*-orientation than $C_6H_5\cdot CCl_3$ and $C_6H_5\cdot CH_2\cdot CCl_3$ respectively, and we propose to study these and the other comparisons mentioned.

only be regarded as approximate; nevertheless, it appears probable that they place the various groups in the correct order, excepting possibly in the cases of some of those which gave closely similar values.

Discussion of Results.

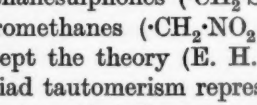
The above group of compounds was selected for study because it appeared likely to yield evidence regarding the three anticipated subsidiary influences already alluded to.

According to Sugden, Reed, and Wilkins (J., 1925, **127**, 1525) the sulphone group contains two semi-polar double linkings, so that the structure of sulphones must be represented thus:

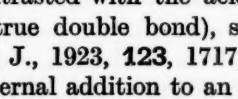


and there is ample chemical evidence that these semi-polar double linkings are not easily depolarised. The static neutral character of methanesulphones ($\cdot CH_2 \cdot SO_2$), contrasted with the acid nature of nitromethanes ($\cdot CH_2 \cdot NO_2$; one true double bond), shows—if we accept the theory (E. H. Ingold, J., 1923, **123**, 1717, *et seq.*) that triad tautomerism represents internal addition to an unsaturated centre—that there is no real or potential unsaturated linking in the sulphone group. Similarly, the non-formation of sulphonamides from sulphonic esters and aqueous ammonia, in contrast to the ready production of carboxylamides from carboxylic esters, accords with the assumed structural difference ($-SO_2 \cdot OMe$, no double bond; $-CO \cdot OMe$, one double bond) if, as Gane and Ingold suggested (J., 1926, 11), aldehyde-ammonia addition is the first stage in the formation of carboxylamides from esters. For these and other reasons, we may regard the valency-octet of sulphur in sulphones as fixed for most reactions, and the charge on the core of the atom (nucleus + 10 electrons) as fixed also.

(i) *Influence of neutral atoms.* Of the simpler available groups, R (R′ = benzyl), the greatest disparity was to be expected (p. 814) between $-CH_3$ and $-F$, but we have not troubled to prepare benzylsulphonyl fluoride because the readily obtained chloride gave a perceptibly higher meta-value than the methyl sulphone:



(meta, 30%)



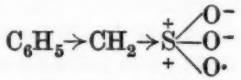
(meta, 51%)

On the other hand, all the other instances investigated (excepting R = OH—see below) yielded values differing only slightly from that given by the methyl sulphone, and from this we may conclude

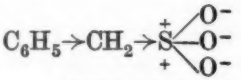
that the fractional charges set up by the varying electron affinities of neutral atoms are insignificant in comparison with such integral ionic charges as the charge inherent in the sulphur atom of a sulphone, excepting in the case of strongly electro-polar atoms such as those of the halogen family.

(ii) *Influence of charged atoms.* Since the meta-value for R = F should be at least as great as that for R = Cl, it will be evident from the above table that $^-$OH falls out of its place in the possible sequence $NH_2 < OH < F$. A rough estimate of the meta-value expected for R = OH [made by noting the value obtained for the methyl ester (R = OMe) and the relationship between the figure for the amide ($R = NH_2$) and those for the substituted amides (R = NHMe, NMe_2, etc.)] would be about 35%, which does lie between the limits set by $R = NH_2$ and Cl; but the observed value (14%) falls far short of this.

The difference, however, is readily interpreted on the grounds that sulphonic acids are strong acids and may be assumed to be almost completely ionised in solution; in other words, the case of benzylsulphonic acid corresponds, not with R = OH, but with R = O′, the depression of the meta-value representing the effect of introducing a third negatively charged oxygen atom in addition to the two already present in the sulphone group. We can call to mind no clearer proof than this of the compensating action of the more remote end of a dipolar group: *



(meta, *ca.* 35%)

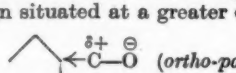


(meta, 14%)

(iii) *Influence of the sulphur electrons.* If the meta-value 35% approximately represents the effect of the two-fold dipole in the sulphone group, the unit dipole contained in a similarly situated sulphoxide group must correspond with a much smaller meta-value, and although we have as yet made no experiments with benzylalkylsulphoxides, we feel sure that under comparable conditions they would not yield more than small proportions (*e.g.*,

* The *op*-substitution of benzoic acid in alkaline solution (Lossen, D.R.-P. 146174), in contrast to its *m*-substitution in acid media, is regarded (see following paper) as an illustration of the reversal of the effect of a *fractional* charge by an *integral* charge of opposite sign situated at a greater distance:

(*meta*-)



(*ortho-para*-).

It follows that benzenesulphonic acid should not show the same marked difference of behaviour under the two conditions, since (unlike benzoic acid) the free acid would be nearly as strong an electrolyte as its salts.

5—10%) of *m*-isomeride. Comparison with the value (50%) established for the unit dipole in the analogously situated nitro-group (p. 814) shows that the effect of a positive ionic charge on sulphur must suffer relatively greater loss within the atom itself than is the case with nitrogen.

EXPERIMENTAL.

(A) *Preparation of Benzylsulphonyl Compounds.*

Benzylmethylsulphone, $C_7H_7 \cdot SO_2 \cdot CH_3$.—Benzylsulphonyl chloride (50 g.) was reduced with zinc dust (24 g.) and boiling alcohol (1000 c.c.) as described by Fromm and Palme (*Ber.*, 1906, **39**, 3312), and the neutralised liquid (70 g. of anhydrous sodium carbonate were used) evaporated to dryness under reduced pressure. The residue was extracted with hot alcohol (1000 c.c.), and the filtered solution evaporated to dryness, also under diminished pressure. The residue from this evaporation was dissolved in 200 c.c. of water, and the filtered solution shaken with 25 c.c. of methyl sulphate at 40° until crystals began to appear. Sodium hydroxide (40 c.c. of 8*N*-solution) was gradually added and the shaking continued until the temperature began to fall; the mixture was then heated to 75°, shaken for a further 15 minutes, and allowed to cool. Yield, 21 g.; m. p. 123—125°. The specimen used for nitration was crystallised first from aqueous alcohol and then from chloroform–ligroin.

Benzylsulphonamide and the Sulphonalkylamides.—The unsubstituted amide was prepared as recommended by Johnson and Ambler (*J. Amer. Chem. Soc.*, 1914, **36**, 380) and purified by crystallisation from water. Benzylsulphonmethylamide, $C_7H_7 \cdot SO_2 \cdot NHMe$, prepared by dissolving the sulphonyl chloride in 33% aqueous methylamine and boiling off most of the excess of the base, separated from aqueous alcohol or from ethyl acetate–ligroin in laminæ, m. p. 108—109° (Found: S, 17·7. Calc.: S, 17·3%). Johnson and Ambler (*loc. cit.*) obtained the same substance along with the dimethylamide (below) by methylation of the simple amide.

Benzylsulphonethylamide, $C_7H_7 \cdot SO_2 \cdot NHEt$, was similarly prepared, excepting that the excess of ethylamine was neutralised with hydrochloric acid, and crystallised first from aqueous methyl alcohol below the ordinary temperature and finally from ether–ligroin, from which it was obtained as leaflets, m. p. 65—66° (Found: S, 16·0. $C_9H_{13}O_2NS$ requires S, 16·1%).

Benzylsulphondimethylamide, $C_7H_7 \cdot SO_2 \cdot NMe_2$, was obtained by means of aqueous dimethylamine, and crystallised first from dilute methyl alcohol and then from chloroform–ligroin; it formed large, thin plates, m. p. 101° (Found: S, 15·9. Calc.: S, 16·1%).

Benzylsulphondiethylamide, $C_7H_7 \cdot SO_2 \cdot NEt_2$, prepared by dissolving the chloride in excess of pure diethylamine and pouring the solution into dilute sulphuric acid, crystallised from ether–ligroin below 0° in leaflets, m. p. 29° (Found: S, 14·2. $C_{11}H_{17}O_2NS$ requires S, 14·1%).

Benzylsulphonic Acid and its Methyl Ester.—The sodium salt of the acid prepared by Johnson and Ambler's method (*loc. cit.*) was crystallised three times from water. The *methyl* ester was prepared by boiling the chloride with a slight deficit of methyl-alcoholic sodium methoxide for 15 minutes, after which the suspension was cooled and mixed with water, and the crystalline precipitate, which contained a little unaltered chloride, was collected and ground for 1·5 minutes with aqueous ammonia (*d* 0·880). The mixture was diluted with water, and the solid was collected, washed with an abundance of cold water, dried, and crystallised from ether; large, lustrous prisms then separated, m. p. 61—62° (Found: C, 52·0; H, 5·2; S, 17·3. $C_{10}H_8O_3S$ requires C, 51·6; H, 5·4; S, 17·2%). On boiling with water for 5 minutes, complete hydrolysis takes place.

Benzylsulphonyl Chloride.—This was prepared as recommended by von Pechmann (*Ber.*, 1873, **6**, 534). The specimen used for nitration was crystallised twice from chloroform–ligroin.

(B) *Nitration of Benzylsulphonyl Compounds and Estimation of the* m-*Isomeride: General Method.*

It was found possible to effect the smooth mononitration of all the substances investigated except one (the diethylamide) under the same set of conditions. The proportion of nitric acid ($d^{18°}$ 1·494) was 1 kg. per g.-mol. of substance, the latter being added in small portions at the uniform rate of 0·2 g. per minute to the rapidly stirred acid at — 10° to — 5°. The mixture was warmed to 0° during 1 hour and then mixed with ice. The method of isolating and separating the nitration product varied with the different examples, but in all cases excepting the methylsulphone, the sulphonic acid, and the diethylamide the pure *m*-isomeride was isolated; in the case of the methylsulphone, it was obtained in an impure condition and in the case of the sulphonic acid it was isolated as a derivative.

For the estimation of the *m*-isomeride, the method of oxidation by permanganate and separation of the nitrobenzoic acids (Baker and Ingold, *loc. cit.*; Goss, Hanhart, and Ingold, *loc. cit.*) was employed, and although the yields of mixed nitrobenzoic acids were not quantitative (they were mostly in the neighbourhood of 80—85%) it was possible to correct for any small disparities in

the percentage conversions of the different isomerides by noting the yields obtained on oxidation of the separated isomerides and of mixtures of them of different composition,* precautions being taken to keep the conditions of oxidation comparable in each group of experiments. In most experiments, partial separation of the original nitration product was effected before oxidation was resorted to.

(C) *Details relating to Individual Cases.*

(*a*) *Benzylmethylsulphone.* — (i) *Qualitative separation.* The nitration product was obtained in a total yield of 97·6%, of which 70·3% was precipitated on the addition of ice and 27·3% was extracted by chloroform from the neutralised filtrate. The precipitated part (Found: C, 45·1; H, 4·0. Calc.: C, 44·7; H, 4·2%) had m. p. 90—140°, and 1·00 g., crystallised from 40 c.c. of benzene, yielded 0·57 g. of a product, m. p. 160—165°, which, crystallised from alcohol, yielded (in two fractions) 0·48 g., m. p. 167—168°. Further crystallisation did not change this m. p., and since oxidation yielded *p*-nitrobenzoic acid, m. p. 234—236° unpurified (mixed m. p. 235—236°), this compound must be p-*nitrobenzylmethylsulphone* (Found: C, 44·4; H, 4·5; N, 6·7. $C_8H_9O_4NS$ requires C, 44·7; H, 4·2; N, 6·5%). The product contained in the mother-liquors, on crystallisation from alcohol and from ethyl acetate–alcohol, gave needles (0·25 g.), m. p. 105—106°, which, although consisting mainly of m-*nitrobenzylmethylsulphone* (Found: C, 44·3; H, 4·5; N, 6·6%), still contained a small proportion of the *p*-isomeride. This was shown by oxidation and separation of the nitrobenzoic acids. The extracted part of the nitration product (Found: C, 44·6; H, 4·2%) had m. p. 75—105°; after three crystallisations from ethyl acetate–alcohol, it gave needles, m. p. 85—87°, consisting (as was shown by oxidation to the nitrobenzoic acids) mainly of o-*nitrobenzylmethylsulphone* (Found: C, 44·5; H, 4·6; N, 6·6%) but contaminated with an appreciable quantity of the *m*-isomeride.

(ii) *Estimation of* m-*isomeride* (Expt. 14). The yield of nitration product was 99·9%, of which 85·7% was precipitated (Found: C, 44·9; H, 4·0. Calc.: C, 44·7; H, 4·2%) and 14·2% extracted

* If $100x$, $100y$, and $100z$ represent the percentage conversions of *o*-, *m*-, and *p*-nitro-isomerides, respectively, and if three mixtures give yields of mixed nitrobenzoic acids amounting to $100Y_1$, $100Y_2$, and $100Y_3$, these products having compositions represented respectively by $100o_1$, $100m_1$, $100p_1$%; $100o_2$, $100m_2$, $100p_2$%; and $100o_3$, $100m_3$, $100p_3$% of *o*-, *m*-, and *p*-nitro-acids, then x, y, and z are given by:

$$x\begin{vmatrix} M_1P_1 1 \\ M_2P_2 1 \\ M_3P_3 1 \end{vmatrix} = y\begin{vmatrix} P_1O_1 1 \\ P_2O_2 1 \\ P_3O_3 1 \end{vmatrix} = z\begin{vmatrix} O_1M_1 1 \\ O_2M_2 1 \\ O_3M_3 1 \end{vmatrix} = \begin{vmatrix} O_1M_1P_1 \\ O_2M_2P_2 \\ O_3M_3P_3 \end{vmatrix}$$

where $O_1 = o_1Y_1$, $O_2 = o_2Y_2$ . . . $M_1 = m_1Y_1$ . . . $P_3 = p_3Y_3$.

with chloroform (Found: C, 44·6; H, 4·2%). The precipitated part on oxidation gave nitrobenzoic acids in 80% yield (*M*, by titration, 167; benzoic acid, by sublimation, nil), which on separation gave 48·9% * of *p*-nitrobenzoic acid, m. p. 234—235°, mixed m. p. 235—236°, and 28·5% * of *m*-nitrobenzoic acid, m. p. 134—138°, mixed m. p. 139—140°. The crude recovered *o*-nitrobenzoic acid (containing *m*-acid) had m. p. 133—143°, mixed m. p. 143—145°, and the total recovery of separated acids was 98·8%. The extracted portion gave nitrobenzoic acids (*M*, 166; benzoic acid, nil) in >74% yield, the exact figure being unknown, as a little of the solution was accidentally lost. Separation gave 9·2% of *p*-acid having m. p. 225—230° (mixed m. p. 230—233°) and 35·7% of *m*-acid, m. p. 133—136° (mixed m. p. 138—141°). The recovered *o*-acid (containing a little *m*-acid) had m. p. 133—137°, mixed m. p. 135—140°.

(Expt. 15.) *p*-Nitrobenzylmethylsulphone was isolated in 34·5% yield, and the residue divided by crystallisation into two fractions amounting to 51·4% and 14·1% of the whole, the total yield in this experiment being quantitative. The first fraction, on oxidation, gave nitrobenzoic acids in 82% yield (*M*, 168; benzoic acid, nil), and these, on separation, gave 9·5% of *p*-acid, m. p. 232—234°, mixed m. p. 234—235°, and 49·4% of *m*-acid, m. p. 130—136°, mixed m. p. 138—140°. The second fraction gave an 81% yield of nitrobenzoic acids (benzoic acid, nil) which on separation yielded 9·4% of *p*-acid, m. p. 224—228°, mixed m. p. 230—234°, and 35·9% of *m*-acid, m. p. 131—134°, mixed m. p. 137—139°.

(Expt. 16.) The yield of nitration product was 98·4%, and from this 38·4% of the theoretical (39·0% of the actual) yield of the pure *p*-isomeride was isolated. The residues, on oxidation, gave nitrobenzoic acids in 84·6% yield (*M*, 167; benzoic acid, nil) which on separation yielded 5·8% of *p*-acid, m. p. 225—230°, and 50·5% of *m*-acid, the precipitated part of which (42·6%) had m. p. 136—137° and mixed m. p. 140°, whilst the part extracted with ether (7·9%) had m. p. 120—130°, mixed m. p. 135—138°.

(Calculations.) From these three experiments we find: para $= 0{\cdot}858 \times 48{\cdot}9 + 0{\cdot}142 \times 9{\cdot}2 = 43{\cdot}3\%$, $34{\cdot}5 + 0{\cdot}514 \times 9{\cdot}5 + 0{\cdot}141 \times 9{\cdot}4 = 40{\cdot}7\%$, $39{\cdot}0 + 0{\cdot}610 \times 5{\cdot}8 = 42{\cdot}6\%$; meta $= 0{\cdot}858 \times 28{\cdot}4 + 0{\cdot}142 \times 35{\cdot}7 = 29{\cdot}5\%$, $0{\cdot}514 \times 49{\cdot}4 + 0{\cdot}142 \times 35{\cdot}9 = 30{\cdot}6$, $0{\cdot}610 \times 50{\cdot}5 = 30{\cdot}8\%$, the disparities in the oxidation conversions being negligible in this case. The mean values are, therefore, para, 42·2%; meta, 30·3%; ortho (by difference), 27·5%.

* These, and all other yields of *p*- and *m*-nitrobenzoic acids recorded in this section are corrected for the solubility of the *p*-acid and the *m*-barium salt (Baker and Ingold, *loc. cit.*).

(*b*) *Benzylsulphonamide.*—(i) ***Qualitative separation.*** Part of the nitration product (28·1%) was precipitated on the addition of ice, and this consisted mainly of *p*-nitrobenzylsulphonamide (Mohr, *Annalen*, 1883, **221**, 218) which was purified by crystallisation from hot water and obtained as clusters of small needles, m. p. 203—204° (Found: C, 39·3; H, 3·8. Calc.: C, 38·9; H, 3·7%). The same substance was obtained by the action of aqueous ammonia on *p*-nitrobenzylsulphonyl chloride. On oxidation, it yielded only *p*-nitrobenzoic acid, m. p. 234—235° (unpurified). The nitric acid solution, on complete evaporation with water, deposited first further quantities of the same isomeride and later the crude *m*-compound as plates, m. p. 150—160°. On recrystallisation, these yielded long, felted needles, m. p. 161°, consisting of pure *m*-nitrobenzylsulphonamide (Purgotti and Monti, *Gazzetta*, 1900, **30**, [ii], 254), as was proved by oxidising them to pure *m*-nitrobenzoic acid, m. p. 139—140° (unpurified), mixed m. p. 139—140°. The same compound was obtained from *m*-nitrobenzylsulphonyl chloride by treatment with aqueous ammonia. It is much more soluble in water than the *p*-amide.

(ii) ***Estimation of the* m-*isomeride*** **(Expt. 21).** The precipitated portion of the nitration product corresponded with 27·8% of the theoretical yield and had m. p. 160—190° (Found: C, 38·5; H, 3·9. Calc.: C, 38·9; H, 3·7%). On oxidation, nitrobenzoic acids (*M*, 166; benzoic acid, nil) were obtained in 83·2% yield, and these on separation gave 82·6% of *p*-acid, m. p. 230—232°, mixed m. p. 231—234°, and *m*-acid which was obtained in two portions, the first (6·7%, precipitated) having m. p. 137—139°, mixed m. p. 140°, and the second (2·2%, extracted with ether) m. p. 125—135°, mixed m. p. 135—140°. The dilute nitric acid solution was evaporated, with several additions of water, to dryness in a vacuum; the residue was not weighed, but, as there was no opportunity for loss, was taken to correspond with 72·2% (Found: C, 38·3; H, 3·7%). Nitrobenzoic acids were obtained in 74·4% yield (*M*, 167; benzoic acid, 0·2%), and their separation gave *p*-acid, m. p. 228—232°, mixed m. p. 230—234° (28·7%), precipitated *m*-acid, m. p. 137—139°, mixed m. p. 140° (30·0%), and extracted *m*-acid, m. p. 125—132°, mixed m. p. 138° (7·5%).

(Expt. 22.) The precipitated portion of the nitration product (28·1%) on crystallisation from water yielded 21·4% of *p*-nitrobenzylsulphonamide (m. p. 203—204°). The residue obtained by evaporating the nitric acid solution was crystallised in successive fractions from water, yielding 9·7% of *p*-amide (m. p. 203—204°), 0·6% of *p*-amide (m. p. 202—204°), and 6·2% of impure *m*-amide (m. p. 150—160°) which, after a further crystallisation, yielded

5·2% of pure *m*-amide (m. p. 161°). All mother-liquors were now combined and evaporated, and the residues (60·7% instead of 63·1%) oxidised as usual. The nitrobenzoic acids (yield, 81·3%; *M*, 166; benzoic acid, nil) on separation gave *p*-acid, m. p. 228—230°, mixed m. p. 232—234° (13·1%); *m*-acid (precipitated), m. p. 136—137°, mixed m. p. 140° (28·5%); and *m*-acid (extracted), m. p. 125—131°, mixed m. p. 136—140° (10·1%).

(Expt. 25.) The precipitated part of the nitration product was crystallised from water, and the filtrate was combined with the dilute nitric acid solution and evaporated, with additions of water, in a vacuum. The *o*- and *m*-amides were extracted with hot water from the sparingly soluble *p*-amide, and were allowed to crystallise after evaporation of the solution to a small bulk; the final filtrate was evaporated to dryness. The yield of *p*-amide (m. p. 203—204°) was 35·6%, of "crystallised mixture" (Found: C, 38·6; H, 3·7. Calc.: C, 38·9; H, 3·7%) 58·7%, and of "evaporated mixture" 5·6% (loss 0·1%). Two independent oxidations of the crystallised mixture gave nitrobenzoic acids in 83·2 and 82·5% yields, respectively, and an average sample of the combined products (*M*, 167; benzoic acid, nil) on separation gave *p*-acid (7·1%), m. p. 220—230°, mixed m. p. 229—232°; *m*-acid (precipitated, 39·6%), m. p. 137°, mixed m. p. 140°; *m*-acid (extracted, 8·6%), m. p. 125—130°, mixed m. p. 135—138°. The nitrobenzoic acids (*M*, 165; benzoic acid, 0·3%) obtained from the evaporated mixture yielded no *p*-acid, and 32·6% of *m*-acid, m. p. 125—135°, mixed m. p. 137—140°, and the *o*-acid recovered had m. p. 130—135° (unpurified), 143—145° (after one crystallisation from chloroform), mixed m. p. 145°.

(Expt. 26.) By a method similar to that used in Expt. 22 the *p*-amide (23·9%, m. p. 203—204°, plus 12·2%, m. p. 202—204°, plus 2·0%, m. p. 200—204°) and *m*-amide (11·6%, m. p. 158—161°) were partly separated, the crop of *m*-amide being obtained by crystallisation from 50% alcohol, and the residues oxidised (yield 83·3%) to nitrobenzoic acids. Separated, these gave 6·2% of *p*-acid, m. p. 225—230°, mixed m. p. 230—232°, and 40·9% of *m*-acid, of which the bulk (precipitated) had m. p. 137—138° (mixed m. p. 140°) and the remainder (extracted), m. p. 124—135° (mixed m. p. 136—139°).

(Calculations.) The isolated *p*-amide on oxidation gave *p*-nitrobenzoic acid in (*a*) 86·0, (*b*) 86·6% yields, and the *m*-amide yielded the *m*-acid in (*a*) 78·1, (*b*) 79·0% yields. A mixture of 0·500 g. of each amide gave mixed acids in 83·2% yield, and these on separation yielded 52·8% of *p*-acid, m. p. 230—233°, and 47·2% of *m*-acid, of which 37·6% had m. p. 136—138° and the remainder

(9·6%) m. p. 124—130°. From these experiments, and the data obtained in Expts. 25 (crystallised mixture) and 26, it is calculated that the percentage conversions of the *o*-, *m*-, and *p*-amides are 87·2, 78·5, and 86·3%, respectively. These figures being used, Expt. 21 gives para, $0{\cdot}278 \times 81{\cdot}8 + 0{\cdot}722 \times 27{\cdot}7 = 42{\cdot}7\%$; meta, $0{\cdot}278 \times 10{\cdot}8 + 0{\cdot}722 \times 39{\cdot}7 = 31{\cdot}7\%$; ortho, 25·6%: Expt. 22 gives para, $31{\cdot}7 + 0{\cdot}631 \times 12{\cdot}7 = 39{\cdot}7\%$; meta, $5{\cdot}2 + 0{\cdot}631 \times 40{\cdot}8 = 31{\cdot}0\%$; ortho, 29·3%: Expt. 25 gives para, $35{\cdot}6 + 0{\cdot}587 \times 6{\cdot}8 = 39{\cdot}6\%$; meta, $0{\cdot}587 \times 50{\cdot}6 + 0{\cdot}057 \times 35 = 31{\cdot}6\%$; ortho, 28·8%: Expt. 26 gives para, $38{\cdot}1 + 0{\cdot}503 \times 6{\cdot}0 = 41{\cdot}1\%$; meta, $11{\cdot}6 + 0{\cdot}503 \times 43{\cdot}2 = 33{\cdot}3\%$; ortho, 25·6%. Since Expt. 26 does not agree well with the other three, it is excluded from the following mean values: Para, 40·7%; meta, 31·4%; ortho (by difference), 27·9%.

(c) *Benzylsulphonmethylamide.*—(i) *Qualitative separation.* The precipitated portion of the nitration product, after crystallisation successively from methyl alcohol, ethyl acetate, and chloroform, gave needles, m. p. 143—145° (Found: C, 41·4; H, 4·4. $C_8H_{10}O_4N_2S$ requires C, 41·7; H, 4·4%), which consisted of p-*nitrobenzylsulphonmethylamide*, since oxidation with permanganate yielded only *p*-nitrobenzoic acid, m. p. 232—234° (unpurified), mixed m. p. 234°. The same methylamide was prepared from the *p*-nitro-chloride and aqueous methylamine. In another experiment, the whole nitration product was extracted with ethyl acetate after neutralisation, and the bulk of the *p*-isomeride allowed to crystallise from this solvent. The mother-liquors on evaporation gave a residue which, on slow crystallisation from methyl alcohol, yielded stellate clusters of needles, m. p. 106—107° (Found: C, 41·4; H, 4·5%). This compound was identified as m-*nitrobenzylsulphonmethylamide*, since, on oxidation with permanganate, it yielded only *m*-nitrobenzoic acid, m. p. 137—140° (unpurified), mixed m. p. 139—140°. It was also prepared from *m*-nitrobenzylsulphonyl chloride and aqueous methylamine.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 32). The diluted nitric acid solution was evaporated in a vacuum, without collection of the precipitated nitro-compounds, and the product oxidised as usual. The nitrobenzoic acids (yield, 76·8%; *M*, 166·5; benzoic acid, nil) gave 42·2% of *p*-acid, m. p. 228—231°, mixed m. p. 230—234°; 21·1% of precipitated *m*-acid, m. p. 134—137°, mixed m. p. 140°; and 7·3% of extracted *m*-acid, m. p. 120—133°, mixed m. p. 134—138°.

(Expt. 36.) The precipitated nitration product (yield 98·4%) was extracted with ethyl acetate after neutralisation (Found: C, 41·6; H, 4·6. Calc.: C, 41·7; H, 4·4%), and after separation

of 32·6% (calculated on the actual yield) of the *p*-isomeride, the remaining amide was oxidised in 82·2% yield to nitrobenzoic acids which on separation gave 10·4% of *p*-acid, m. p. 234—235°, 33·7% of precipitated *m*-acid, m. p. 134—137°, mixed m. p. 139—140°, and 73% of extracted *m*-acid, m. p. 123—136°, mixed m. p. 137—140°.

(Expt. 37.) The product isolated by complete evaporation was separated by crystallisation, giving 29·5% of *p*-methylamide of m. p. 138—141°, 6·2% of m. p. 138—140° and 1·7% of m. p. 137—139°, and 6·8% of *m*-methylamide, m. p. 99—101°. A mixture of the second and third specimens of *p*-compound gave only *p*-nitrobenzoic acid, m. p. 230—234°, and the separated *m*-compound yielded only *m*-nitrobenzoic acid, m. p. 137—139°, on oxidation. Oxidation of the residues was effected in 83·5% yield, and the nitrobenzoic acids (*M*, 166; benzoic acid, 0·9%) on separation gave 11·0% of *p*-acid, m. p. 220—230°, mixed m. p. 227—232°; 29·5% of precipitated *m*-acid, m. p. 134—135°, mixed m. p. 141°; and 9·0% of extracted *m*-acid, m. p. 122—130°, mixed m. p. 135—140°.

(Calculations.) The isolated *p*- and *m*-methylamides gave corresponding nitrobenzoic acids in 85·2 and 80·5% yields, respectively, and it is calculated from Expts. 36 and 37 that the *o*-compound would give about 84·0% under the same conditions. Hence, para = 41·5%, $32·6 + 0·674 \times 10·2 = 39·5\%$, $37·4 + 0·558 \times 11·3 = 43·7\%$; meta = 29·5%, $0·674 \times 42·3 = 28·5\%$, $6·8 + 0·558 \times 39·8 = 29·0\%$. The mean values are: Para, 41·5%; meta, 29·0%; ortho (by difference), 29·5%.

(*d*) *Benzylsulphonethylamide.*—(i) *Qualitative separation.* The precipitated portion of the nitration product was rubbed with a little cold methyl alcohol, and the sparingly soluble portion crystallised from this solvent in needles, m. p. 110—111°. These consisted of p-*nitrobenzylsulphonethylamide* (Found: C, 44·2; H, 5·1. $C_9H_{12}O_4N_2S$ requires C, 44·3; H, 4·9%), since on oxidation they yielded only *p*-nitrobenzoic acid, m. p. 230—234° (unpurified). The same substance was also prepared from *p*-nitrobenzylsulphonyl chloride and aqueous ethylamine. m-*Nitrobenzylsulphonethylamide* was isolated in small amount by fractional crystallisation of the residues from dilute methyl alcohol. It formed stellate bunches of needles, m. p. 90—91° (Found: C, 44·0; H, 5·2%), and on oxidation gave only *m*-nitrobenzoic acid, m. p. 137—139° (unpurified), mixed m. p. 139—140°. The same isomeride was prepared from *m*-nitrobenzylsulphonyl chloride and aqueous ethylamine.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 42). The residue from the diluted and evaporated solution (Found: C, 44·2;

H, 5·1%) was oxidised in 78·4% yield to nitrobenzoic acids (*M*, 167; benzoic acid, 0·9%) which on separation (after removal of the benzoic acid) gave 42·8% of *p*-acid, m. p. 225—230°, mixed m. p. 228—232°; 20·6% of precipitated *m*-acid, m. p. 135—137°, mixed m. p. 140°; and 7·1% of *m*-acid, m. p. 125—132°, mixed m. p. 135—140°, which was extracted with ether.

(Expt. 45.) The *p*-ethylamide (36·6%), m. p. 108—110°, was separated by means of methyl alcohol, and the residues were oxidised to the mixed acids (yield, 79·0%; *M*, 165·5; benzoic acid, nil) which on separation gave 10·9% of *p*-acid, m. p. 224—228°, mixed m. p. 227—231°, 33·7% of precipitated *m*-acid, m. p. 134—139°, mixed m. p. 140°, and 10·4% of *m*-acid, m. p. 124—130°, mixed m. p. 136—140°, extracted with ether.

(Expt. 47.) Preliminary separation gave 32·4% of *p*-amide, m. p. 108—111°, 5·7% of m. p. 107—109°; and 8·1% of *m*-amide, m. p. 86—89°, and 0·6%, m. p. 85—87°. The residues yielded nitrobenzoic acids (yield, 81·0%; *M*, 167; benzoic acid, nil), which on separation gave 6·8% of *p*-acid, m. p. 228—230°, mixed m. p. 230—234°, and 36·7% of *m*-acid, of which 28·5% (precipitated) had m. p. 135—138° and 8·2% had m. p. 125—130° (mixed m. p.'s 140° and 138—139°, respectively).

(Calculations.) The isolated *p*- and *m*-ethylamides gave the corresponding nitrobenzoic acids in 80·4 and 79·1% yields, respectively, and the yields obtained from mixtures were all of this order. Hence the experiments cited give para: 42·8%, $36·6 + 0·634 \times 10·9 = 43·6\%$, $38·1 + 0·532 \times 6·8 = 41·9\%$; meta: 27·5%, $0·634 \times 44·1 = 28·0\%$, $8·7 + 0·532 \times 26·7 = 28·2\%$, the means being: para, 42·8%; meta, 27·9%; ortho (by difference), 29·3%.

(*e*) *Benzylsulphondimethylamide.*—(i) ***Qualitative separation of isomerides.*** The precipitated part of the nitration product, crystallised first from methyl alcohol and then from ethyl alcohol, gave leaflets, m. p. 167°, consisting of p-*nitrobenzylsulphondimethylamide* (Found: C, 44·6; H, 4·7. $C_9H_{12}O_4N_2S$ requires C, 44·3; H, 4·7%). On oxidation by permanganate, it yielded only *p*-nitrobenzoic acid, m. p. 233—234° (unpurified), and it was identical with the substance obtained by dissolving *p*-nitrobenzylsulphonyl chloride in aqueous dimethylamine. m-*Nitrobenzylsulphondimethylamide* was obtained from the mother-liquors as leaflets, m. p. 116—119°, which was not depressed by admixture with a specimen, m. p. 118—119°, obtained from the pure *m*-nitro-chloride (Found: C, 44·3; H, 5·1%). The substance was oxidised by permanganate to *m*-nitrobenzoic acid, m. p. 137—140° (unpurified), mixed m. p. 139—140°.

(ii) ***Estimation of the proportion of* m-*isomeride* (Expt. 52).** The

whole nitration product obtained by dilution and evaporation in a vacuum (Found: C, 44·0; H, 4·4%) was oxidised in 76·7% yield to mixed acids (*M*, 166; benzoic acid, 0·2%) which on separation gave 44·5% of *p*-acid, m. p. 225—233°, mixed m. p. 230—235°, and 27·5% of *m*-acid, of which the bulk (precipitated) had m. p. 138°, mixed m. p. 141°, and the remainder, extracted with ether, m. p. 120—130°, mixed m. p. 136—139°.

(Expt. 55.) The *p*-derivative was isolated in 31·1% yield, m. p. 164—166°, and the residues oxidised in 70·1% yield to mixed acids, which on separation gave 16·7% of *p*-acid, m. p. 230—232°, mixed m. p. 234—235°, and 39·6% of *m*-acid, of which 30·0% had m. p. 133—137°, mixed m. p. 139—140°, and 9·6% had m. p. 125—130°, mixed m. p. 135—138°.

(Expt. 57.) A series of crystallisations yielded 33·7% of the *p*-compound, of which 26·7% had m. p. 164—166° and 7·0% m. p. 163—165°, and 10·6% of *m*-compound, of which 10·3% had m. p. 114—117° and the remainder m. p. 112—116°. The residues (55·0% instead of 55·7%) on oxidation gave nitrobenzoic acids (yield 74·7%) which on separation gave 17·9% of *p*-nitrobenzoic acid, m. p. 220—230°, mixed m. p. 230—234°, and 34·2% of *m*-acid, of which the bulk (precipitated) had m. p. 132—137°, mixed m. p. 139—140°, and the remainder m. p. 120—130°, mixed m. p. 136—139°.

(Calculations.) Independent oxidations of the *p*-compound gave 78·9 and 79·4% yields, and of the *m*-compound 73·8 and 75·6% yields, whence from Expt. 57 the *o*-isomeride should give a 73·3% yield under the same conditions. Hence the data given lead to para: 43·8%, $31·1 + 0·689 \times 15·6 = 41·8\%$, $33·7 + 0·557 \times 16·8 = 43·0$; meta: 28·1%, $0·689 \times 39·8 = 27·5\%$, $10·6 + 0·557 \times 34·3 = 29·7\%$. The mean values are therefore: para, 42·9%; meta, 28·4%; ortho (by difference), 28·7%.

(*f*) *Benzylsulphondiethylamide.*—Difficulty was experienced with the nitration of this substance owing to its tendency to oxidise, but in one experiment (63) it was shown that nitration occurs in the *m*-position to a substantial extent. The substance (1·500 g., this small amount being used owing to the difficulty of keeping the temperature down when oxidation sets in if larger quantities are employed) was nitrated at $-10°$ to $-5°$ as usual, and the solution, after being kept for 10 minutes, was mixed with ice and sodium carbonate solution and extracted with ether. The extract was concentrated without drying, and when the bulk was small, water was added and the solution was boiled to expel the remainder of the ether and treated with permanganate. The mixed acids (yield, 53·7% calculated as nitrobenzoic acids on the basis of the

diethylamide used for nitration) lost 8·6% of their weight at 100°, and the residual mixed nitro-acids (*M*, 166) consisted, as was found by separation, of 47·2% of *p*-nitro-acid, m. p. 220—225°, mixed m. p. 228—233°; 25·1% of *m*-acid, of which the bulk (precipitated) had m. p. 133—135°, mixed m. p. 138—141°, and the remainder (extracted) had m. p. 115—125°, mixed m. p. 132—139°; and (by difference) 27·7% of *o*-acid. The recovered *o*-acid, crystallised once from chloroform, had m. p. 140—146°, mixed m. p. 144—145°. These figures, namely, para, 47·2%; meta, 25·1%; ortho, 27·7%, are regarded as an approximation to the proportions of the nitro-diethylamides originally formed.

(*g*) *Benzylsulphonic Acid.*—This substance has been nitrated by Böhler (*Annalen*, 1870, **154**, 55), who, however, obtained no individual substance, and by Mohr (*loc. cit.*), who showed that the *p*-nitro-derivative was the principal product and that the *o*-isomeride was also formed; the *m*-isomeride was not detected.

(i) *Qualitative examination.* The solution obtained by adding sodium benzylsulphonate to nitric acid under the usual conditions was evaporated in a vacuum after the addition of water, and the residue was crystallised from aqueous alcohol; sodium *p*-nitrobenzylsulphonate (Purgotti and Monti, *loc. cit.*) was then obtained. On oxidation it yielded only *p*-nitrobenzoic acid, m. p. 232—234° (unpurified). The mother-liquors were evaporated, and the residues were washed with a little aqueous alcohol, which removed part of the very soluble sodium *o*-nitrobenzylsulphonate, and treated with phosphorus oxy- and penta-chlorides at 90° for 0·5 hour. The sulphonyl chlorides, collected after decomposition with water of the excess of phosphorus chlorides, when crystallised from chloroform–ligroin, gave *m*-nitrobenzylsulphonyl chloride as plates, m. p. 101°, which in some fractions were mixed with prisms from which they could be mechanically separated. On hydrolysis, they yielded Purgotti and Monti's *m*-nitrobenzylsulphonic acid (*loc. cit.*).

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 72). The well-dried nitration product was converted into the mixed chlorides with phosphorus penta- and oxy-chlorides at 90°, and the chlorides transformed by ammonia in dry ether into the amides, which were oxidised. The nitrobenzoic acids (yield, 74·6% calculated on the original sodium benzylsulphonate; *M*, 166; benzoic acid, nil) on separation gave *p*-acid (53·9%), m. p. 227—233°, mixed m. p. 230—235°, and *m*-acid (12·5%), the greater portion of which had m. p. 135—137° (mixed m. p. 139—140°) and the remainder m. p. 125—131° (mixed m. p. 136—140°). The recovered *o*-acid (33·6%; loss nil) after one crystallisation from chloroform had m. p. 140—143°, mixed m. p. 143—146°.

(Expt. 73.) The same method being followed initially, the nitro-chlorides (93·7% yield) were prepared, and crystallised from chloroform–ligroin; 29·3% of the *p*-nitro-chloride (prisms, m. p. 89—90°) were then separated. The mother-liquors yielded a small crop (2·2%) of the *m*-derivative (plates, m. p. 99—100·5°). The remaining material was converted into amides and oxidised in 76·0% yield (calculated on the nitro-chlorides) to mixed acids (*M*, 167; benzoic acid, nil), which on separation gave 33·7% of *p*-acid, m. p. 225—231°, mixed m. p. 230—235°, and 16·0% of *m*-acid, of which 11·0% (the precipitated part) had m. p. 135—137°, mixed m. p. 139—140°, the remainder having m. p. 125—131°, mixed m. p. 135—138°.

(Expt. 74.) The method was the same as in Expt. 72, and the separation yielded 54·6% of *p*-acid, m. p. 230—231°, mixed m. p. 231—234°, and 12·8% of *m*-acid (isolated altogether), m. p. 130—132°, mixed m. p. 137—140°.

(Expt. 75.) The method of Expt. 73 being adopted initially, the chlorides were separated, yielding 23·7% of *p*-chloride (m. p. 89—90°) and 3·1% of *m*-chloride (m. p. 98—100°), and the residues converted into amides, which on partial separation yielded 9·8% of *p*-amide (m. p. 200—203°). The final residues on oxidation gave nitrobenzoic acids (yield, 70·7%; *M*, 166; benzoic acid, 0·5%), which on separation yielded 29·7% of *p*-acid, m. p. 225—230°, mixed m. p. 230—234°, and 14·6% of *m*-acid, of which the bulk (precipitated) had m. p. 130—136°, mixed m. p. 139—140°, and the remainder (extracted) m. p. 120—130°, mixed m. p. 136—139°. The recovered *o*-acid, after one crystallisation from chloroform, had m. p. 141—143°, mixed m. p. 143—145°.

(Calculations.) From the previously determined oxidation-conversions of the amides, the following values are calculated: para = 53·2%, $29·3 + 0·685 \times 33·1 = 52·0\%$, 54·0%, $33·5 + 0·634 \times 29·2 = 52·0\%$; meta = 13·6%, $2·2 + 0·685 \times 17·4 = 14·1\%$, 13·9%, $3·1 + 0·634 \times 15·8 = 13·1\%$. Thus, the mean values are: para, 52·8%; meta, 13·7%; ortho (by difference), 33·5%.

(*h*) *Methyl Benzylsulphonate.*—(i) *Qualitative separation of isomerides.* Almost the whole of the nitration product was precipitated, on the addition of ice, as an oil which soon solidified. *Methyl* p-*nitrobenzylsulphonate* was readily separated by grinding the mixture with ether and crystallising the undissolved portion from ethyl acetate–ligroin, from which it separated in small, hard cubes, m. p. 113° (Found: C, 41·7; H, 3·8. $C_8H_9O_5NS$ requires C, 41·6; H, 3·9%). On oxidation by permanganate, it was converted almost quantitatively into *p*-nitrobenzoic acid, m. p. 234—235°

(unpurified). Probably hydrolysis precedes oxidation, since boiling with water for a short time converts the ester into the free sulphonic acid and methyl alcohol. By crystallising the part which dissolved in ether from ethyl acetate–ligroin, methyl *m*-nitrobenzylsulphonate was obtained as thin, rhomboidal leaflets, m. p. 99—100° (Purgotti and Monti, *loc. cit.*, record m. p. 77°), and a further quantity of the same isomeride was obtained from the mother-liquors of the *p*-compound by mechanical separation of the crystals (Found: C, 41·2; H, 3·9%). The orientation was proved by boiling with water, evaporating the neutralised solution of the sulphonic acid to dryness, and digesting the residue with phosphorus pentachloride and oxychloride at 90° for a few minutes; *m*-nitrobenzylsulphonyl chloride (m. p. 100—101°) was then obtained.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 83). The precipitated nitration product (yield 94%) was hydrolysed by boiling with water and the nitrosulphonic acids were converted into their amides as in the preceding series of experiments, and oxidised in that form. The mixed acids gave 47·0% of *p*-acid, m. p. 210—220°, mixed m. p. 220—230°, and 28·0% of *m*-acid, m. p. 127—130°, mixed m. p. 135—140°.

(Expt. 84.) The nitration product was extracted with ethyl acetate (yield 95%) and treated as in the preceding experiment. The nitrobenzoic acids gave 42·3% of *p*-acid, m. p. 225—231°, mixed m. p. 228—234°, and 31·2% of *m*-acid, of which 25·9% (precipitated) had m. p. 137—139°, mixed m. p. 139—140°, and the remainder (extracted) m. p. 122—129°, mixed m. p. 136—138°.

(Expt. 87.) The *p*-nitro-derivative was partly separated from the nitration product by means of ether and ethyl acetate (29·0% having m. p. 113°, and 4·3% having m. p. 110—113°), and the residues were converted into amides and oxidised. The acids gave 13·2% of *p*-acid, m. p. 230—232°, mixed m. p. 234—235°, and 48·1% of *m*-acid, of which 37·9% had m. p. 138—139°, mixed m. p. 140°, and the remainder had m. p. 125—130°, mixed m. p. 136—137°.

(Calculations.) Using the oxidation data for the amides, we have para = 45·7%, 41·0%, 33·3 + 0·667 × 12·7 = 41·8%; meta = 29·9%, 33·5%, 0·667 × 50·5 = 33·7%, and the means are: para, 42·9%; meta, 32·4%; ortho (by difference), 24·7%.

(*i*) *Benzylsulphonyl Chloride.*—(i) *Qualitative separation.* The nitration product was completely precipitated on addition of ice, and the bulk of the *m*-nitro-derivative was readily separated as leaflets, m. p. 100—101° (compare Purgotti and Monti, *loc. cit.*), by crystallisation from chloroform–ligroin (4 : 1 by vol.) (Found: C, 36·1; H, 2·8%). Its identity was shown by conversion into the

m-amide and by oxidation to *m*-nitrobenzoic acid. *p-Nitrobenzylsulphonyl chloride* was obtained from the mother-liquors as large, inclined prisms, m. p. 90° (Found: C, 36·1; H, 2·7. $C_7H_6O_4NClS$ requires C, 35·7; H, 2·6%). On oxidation with permanganate it yielded only *p*-nitrobenzoic acid, m. p. 230—234° (unpurified), and on treatment with ammonia gave the *p*-nitro-amide.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 92). The precipitated nitration product (yield 96·9%) (Found: C, 35·7; H, 2·8. Calc.: C, 35·7; H, 2·6%) was crystallised from 1·5 parts by weight of chloroform mixed with one-quarter of its volume of ligroin; 38·4% (calculated on the yield *isolated*) of pure *m*-compound, m. p. 100—101°, then separated. The residues, on conversion into the amides and on oxidation gave nitrobenzoic acids (*M*, 166; benzoic acid, nil) which, when separated, were found to consist of 53·2% of *p*-acid, m. p. 222—230°, mixed m. p. 230—234°; 20·5% of *m*-acid, m. p. 133—135°, mixed m. p. 138°; and 26·3% of *o*-acid (by difference).

(Expt. 93.) The whole product was converted into amides and oxidised to mixed acids (*M*, 167; benzoic acid, nil) which on separation gave 36·7% of *p*-acid, m. p. 220—230°, mixed m. p. 230—232°, and 45·9% of *m*-acid, of which 30·0% had m. p. 136—137°, mixed m. p. 140°, and 15·9% had m. p. 120—130°, mixed m. p. 135—139°.

(Expt. 96.) Fractional crystallisation from chloroform–ligroin containing gradually increasing proportions of ligroin gave 39·8% of *m*-chloride, m. p. 99·5—101°, 3·0% having m. p. 99—100°, and 0·3% having m. p. 97—99°, together with 9·1% of *p*-chloride, m. p. 88—90°, and 0·2% having m. p. 87—89°. The residues, on oxidation after conversion into amides, gave nitrobenzoic acids (yield, 80·0%; *M*, 166; benzoic acid, nil) which, when separated, yielded 49·5% of *p*-acid, m. p. 224—232°, mixed m. p. 230—234°, and 17·0% of *m*-acid, of which 10% had m. p. 134—138°, mixed m. p. 140°, and 7% had m. p. 125—130°, mixed m. p. 136—139°.

(Calculations.) By the method already illustrated, the above data gave para: $0{\cdot}616 \times 52{\cdot}2 = 32{\cdot}1\%$, 34·8%, $9{\cdot}3 + 0{\cdot}476 \times 48{\cdot}7 = 32{\cdot}5\%$; meta: $0{\cdot}616 \times 22{\cdot}1 = 52{\cdot}0\%$, 48·6%, $43{\cdot}1 + 0{\cdot}476 \times 18{\cdot}4 = 51{\cdot}9\%$. The means, neglecting Expt. 93, are: para, 32·3%; meta, 52·0%; ortho (by difference), 15·7%. The means, including Expt. 93, are: para, 33·1%; meta, 50·8%; ortho (by difference), 16·9%.

(D) *Summary of Results.*

The following tabular summary is appended for convenience in reference:—

Nitration of Benzylsulphonyl Compounds by Nitric Acid ($d^{18°}$ 1·494) at − 10° to − 5°.

R in directing group, $CH_2{\cdot}SO_2{\cdot}R$.	Isomerides formed (%).				
	Para.	Mean.	Ortho.	Meta.	Mean.
CH_3	43·3 40·7 42·6	42·2	27·5	29·5 30·6 30·8	30·3
NH_2	42·7 39·7 39·6	40·7	27·9	31·7 31·0 31·6	31·4
NHMe	41·5 39·5 43·7	41·5	29·5	29·5 28·5 29·0	29·0
NHEt	42·8 43·6 41·9	42·8	29·3	27·5 28·0 28·2	27·9
NMe_2	43·8 41·8 43·0	42·9	28·7	28·1 27·5 29·7	28·4
NEt_2	47·2	47·2	27·7	25·1	25·1
OH (doubtless ionised)	53·2 52·0 52·0	52·8	33·5	13·6 14·1 13·1	13·7
OMe	45·7 41·0 41·8	42·9	24·7	29·9 33·5 33·7	32·4
Cl	32·1 34·8 32·5	33·1	16·9	52·0 48·6 51·9	50·8

The figures recorded in the last column are rounded in the abridged table given in the introduction.

THE UNIVERSITY, LEEDS. [*Received, December 16th*, 1926.]

CXX.—*The Nature of the Alternating Effect in Carbon Chains. Part XV. The Directive Action of Some Groups of the Form* –CR′R″·COR *in Aromatic Substitution.*

By JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD.

WHEN two atoms having corresponding electronic systems in the combined state, but different nuclear charges, are directly united, it is to be expected that the electrons concerned in the union will be more strongly attracted by the more powerful positive nucleus. Thus, carbon and oxygen in the combined state both possess

10 electrons, and their nuclear charges are in the ratio 6 : 8; * hence the electrons of the bond C—O will be more under the influence of the oxygen than of the carbon nucleus. In other words, the oxygen atom will have more than a half-share in these shared electrons, and so on the whole it will be feebly negatively charged. Similarly, the carbon atom, possessing less than a half-share in the same pair of electrons, will on the whole be feebly positively charged: $\overset{\delta+}{C}—\overset{\delta-}{O}$. The electric moment of this fractional dipole will, of course, be very small, but in a double bond, where the electrons are assumed to be more loosely held, the separation of $\pm$ charges consequent on an unequal nuclear attraction should be greater and the effects traceable to dipolar character correspondingly enhanced.† Thus it follows that so-called non-polar (4-electron) double bonds, such as the carbonyl bond, in which there is reason to suspect an unequal sharing of the electrons, should display to a small, but possibly detectable, extent those properties which are so strikingly characteristic of the semi-polar (2-electron) double bond and depend on the creation of an electrical field.

(I.) $—\overset{+}{N}\rightleftharpoons\overset{-}{O}$ $\qquad\qquad$ $—\overset{\delta+}{C}=\overset{\delta-}{O}$ (II.)

The capacity of the semi-polar double linking (I) for producing *m*-substitution, when its positive end is separated from the benzene nucleus by a saturated carbon atom, is well illustrated by the large degree of *m*-substitution observed in the nitration of phenylnitromethane derivatives (Baker and Ingold, J., 1926, 2462; this vol., p. 261); it has been confirmed by the study of benzylsulphonyl compounds (see Part XIV).

Probably the *m*-orientation effects observed in benzoyl compounds (*e.g.*, benzaldehyde, acetophenone, benzoic acid and its esters) are to be attributed, in part at least, to the occurrence of the fractional dipole (II) in the resting state of the carbonyl group, but in these cases other mechanisms are possible, depending on the alternation of single with double linkings. In phenylacetyl compounds, however, such mechanisms are excluded, and any *m*-nitration, beyond the 3% observed in the case of toluene,‡ must arise

* The screening effect of the inner pairs of electrons will tend to increase the effective disparity, which will also be somewhat influenced by more distant electronic and nuclear charges.

† The permanent fractional dipole moments should be in the order C=O> C=N and C—F>C—O>C—N in the absence of poles and other powerful disturbances.

‡ For reasons given previously (J., 1926, 2462), toluene is taken as the standard of reference in the comparisons represented by :

$C_6H_5\cdot CH_2\leftarrow X$ (meta<3%) $\qquad$ $C_6H_5\cdot CH_2—H$ (meta = 3%) $\qquad$ $C_6H_5\cdot CH_2\rightarrow Y$ (meta>3%)

from the permanent dipole. We have therefore studied the nitration of ethyl phenylacetate and are able to show that it forms approximately 9% of *m*-nitro-derivative (IV). To confirm the matter, we have also examined the nitration of ethyl phenylmalonate,* in which the electron-attraction in the side-chain would be expected to be about twice as great, and in this case we find 20% of *m*-derivative (V).

The value for ethyl phenylacetate (IV) may be contrasted with that previously recorded for phenylnitromethane (III) :

$C_6H_5\cdot CH_2\cdot NO_2$	$C_6H_5\cdot CH_2\cdot CO_2Et$	$C_6H_5\cdot CH(CO_2Et)_2$
(meta, 50%)	(meta, 9%)	(meta, 20%)
(III.)	(IV.)	(V.)

Experimental.

Nitration of Ethyl Phenylacetate.—Radziszewski (*Ber.*, 1869, **2**, 209; 1870, **3**, 648) nitrated this substance and established the formation of the *o*- and *p*-nitro-derivatives.

The ester was run slowly into 6 vols. of nitric acid (*d* 1·50) at 0° and the product was kept at 0° for a further 4 hours, then mixed with ice, and basified with potassium hydroxide. The precipitated nitro-products were collected, washed with cold water, and dried in ethereal solution, to which the ethereal extract of the mother-liquor was added. After analysis, the mixed nitro-compounds were oxidised to nitrobenzoic acids, in which the proportion of *m*-isomeride was determined either by titration (Baker, this vol., p. 565) or by separation (Baker and Ingold, *loc. cit.*).

(Expt. 12.) From 5·350 g. of the ester, 6·174 g. (92%) of nitro-derivatives (Found : C, 57·3; H, 5·4. Calc. : C, 57·4; H, 5·3%) were obtained; a further 6% of the material was accounted for as acid by-products formed by oxidation or hydrolysis. The yield of nitrobenzoic acids was 95% (Found : *M*, 165·6. Calc., 167). On titration, 1·2374 g. required 73·68 c.c. of 0·01029*N*-baryta for the neutralisation of the *m*-acid, corresponding with 0·1266 g. of *m*-nitrobenzoic acid, which when corrected becomes 0·110 g., or 9·3%.

* The choice of these compounds for study requires some explanation. Benzyl alkyl ketones were ruled out owing to probable disturbances arising from the presence of enols of the type $C_6H_5\cdot CH{:}C(OH)\cdot R$; phenylacetic and phenylmalonic acids should give higher proportions of *m*-derivative than their respective esters *if substitution were to occur exclusively in the undissociated forms*, but, since only a small effect was being sought for, there was no guarantee that the contrary influence of ionisation (preceding paper) would be negligible; the same is true of the influence of alkyl groups in ketones such as $C_6H_5\cdot CMe_2\cdot COR$; consequently the esters examined belong to one of the few classes of compounds suitable to our purpose.

(Expt. 13.) The yield from 10·00 g. was 12·038 g. (96%) (Found: C, 57·3; H, 5·6%), and partial separation prior to oxidation of the unseparated part was effected as follows. An average sample (5·044 g.) was crystallised from ethyl alcohol, yielding 1·038 g. of ethyl *p*-nitrophenylacetate, m. p. 62°, and the residues from the mother-liquor were again crystallised from a small quantity of the same solvent, giving 0·382 g. of the same isomeride, m. p. 60—62° (total, 1·42 g. = 28·2%). From these fractions, by oxidation, *p*-nitrobenzoic acid, m. p. 234° (unpurified; either alone or mixed with a genuine specimen), was obtained in 87% yield. 3·390 G. of the unseparated residues were similarly oxidised in 87·4% yield to nitrobenzoic acids, and on acidification of the alkaline solution 0·667 g. of *p*-nitrobenzoic acid, m. p. 234°, mixed m. p. 234°, crystallised and was collected. Extraction with ether gave 1·680 g. of mixed acids (benzoic acid, 1·1%), 1·500 g. of which, on separation, gave a further 0·262 g. of *p*-nitrobenzoic acid (solubility correction, 0·025 g.) and two fractions of *m*-acid, one of which (0·178 g.) had m. p. 128° and the other (0·139 g.) m. p. 123°, with previous softening in each case (barium salt solubility correction, 0·045 g.). Since these m. p.'s are lower than are usually observed for *m*-acid isolated in similar separations of artificial mixtures, the two fractions were crystallised from ethyl acetate–ligroin, giving 0·152 g. of pure *m*-acid, to which the barium salt solubility correction must be added together with half the weight of the impure residues. Hence the original nitration product contained: para, 28 + 20 + 10 = 58%; meta, 9·5 ± 2·5%; ortho (by difference), 32·5 ± 2·5%.

The figure for the *p*-isomeride was confirmed by an independent nitration (yield 91%, analysis correct, yield on oxidation 93%), which gave para, 59%.

Nitration of Ethyl Phenylmalonate.—The ester (Found: C, 65·4; H, 6·5. Calc.: C, 66·0; H, 6·8%) was prepared by thermal decomposition of ethyl phenyloxaloacetate, which was obtained by condensing ethyl phenylacetate with ethyl oxalate (Wislicenus, *Annalen*, 1888, **246**, 315).

(Expt. 23.) The ester was run slowly into 6 vols. of nitric acid (*d* 1·49) at − 15° to − 10° at the rate of 1 g. per hour, and after being kept for a further hour at the same temperature the mixture was poured on to ice, nearly neutralised with potassium hydroxide, and then completely neutralised with sodium carbonate. The nitration product, a yellow oil, was extracted with ether (Found: C, 54·2; H, 5·1. Calc.: C, 55·5; H, 5·4%) and oxidised with permanganate, and the nitrobenzoic acids were isolated in the usual manner (yield, 90%; *M*, 165·3). 0·4633 G. required 60·96 c.c. of 0·01029*N*-barium hydroxide to neutralise the *m*-acid, corre-

sponding with 0·1065 g., which when corrected becomes 0·0935 g., of this isomeride, that is, 20·2%.

Another portion of the mixed acids after removal of the benzoic acid (1·8%) by sublimation was treated as in Expt. 13, and gave 47% of *p*-acid and 21 ± 5% of *m*-acid; *o*-acid (by difference), 32 ± 5%.

(Expt. 25.) The yield of nitro-compounds from 3·623 g. was 4·161 g. (90%) (Found: C, 54·5; H, 5·4%), which on oxidation gave 0·333 g. of *p*-nitrobenzoic acid (crystallised from the aqueous solution) and 1·151 g. of mixed acids (extracted with ether) (*M*, 168). The extracted portion (0·979 g.) gave 0·142 g. (crystallised) of *m*-nitrobenzoic acid, m. p. 135°, mixed m. p. 140°, and 0·049 g. (extracted with ether), m. p. 115°, mixed m. p. 128—130°. The *p*-acid was accidentally lost before weighing. For the original nitration product, meta = 18%.

Summary.—The above results are collected together in tabular form:

Nitration of Ethyl Phenylacetate and Ethyl Phenylmalonate in Nitric Acid (d 1·5).

Side-chain.	Temp. (mean).	Proportions by separation (%) (corrected for solubilities). *Para*-.	*Meta*-.	% *Meta*- (by estimation).	Mean % *meta*-.
$-CH_2\cdot CO_2Et$	± 0°	58, 59	9·5	9·3	9
$-CH(CO_2Et)_2$	−12·5	47	18, 21	20·2	20

We desire to thank the Royal Society for defraying part of the expense incurred in this investigation.

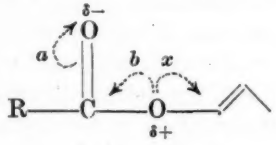
THE UNIVERSITY, LEEDS. [*Received, December 21st*, 1926.]

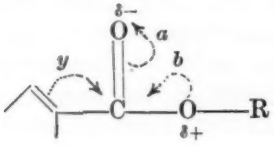
CXXI.—*The Nature of the Alternating Effect in Carbon Chains. Part XVI. The Directive Action of Some Groups of the Form* –COR *in Aromatic Substitution.*

By KENNETH ERNEST COOPER and CHRISTOPHER KELK INGOLD.

IN Part V (J., 1926, 1310), Ingold and Ingold considered the diminution in the *op*-directive power of a phenoxyl oxygen atom arising from its attachment to a carbonyl group (R·CO·OPh) and attributed the effect to the establishment of a weak electrovalency between the carboxyl oxygen atoms, thus adapting a previous theory (Smedley, J., 1909, 95, 231) of the structure of the carboxyl

group. Expressed in terms of electron-strain transmission, the conception (I) was that the process (*b*), actuated by (*a*), competes with the process (*x*) to which the *op*-directing action of the group is due; or, in other words, that the charge $\delta +$, set up by (*a*) and (*b*) together, works against the repulsion of electrons towards the nucleus :

I.) 



(II.)

At first sight it might appear to follow that the *m*-directive power of a benzoyl carbonyl-group should be decreased by its attachment to a hydroxylic or ethereal oxygen atom (Ph·CO·OR) for a precisely similar reason (II): the demand created by process (*a*) can be supplied, not only by (*y*) leading to *m*-substitution, but also by (*b*), which therefore works against *m*-substitution. At least it seems that there can be no escape from this conclusion for any theory which regards the "conjugation" of the carbonyl group with the nucleus as the sole cause of its *m*-directive effect.

On the other hand, if the view (this vol., p. 833) be adopted that the action of the carbonyl group in benzoyl compounds (to illustrate by this example) arises largely from permanent electron-strain (J., 1926, 2442, 2463; this vol., pp. 813–815) set up by the fractional dipole in the resting state of the carbonyl group, then, whilst the conclusion represented by (I) remains (for the charge $\delta +$ created by strains *a* and *b* must necessarily oppose *op*-substitution), that represented by (II) becomes inverted. For each of the bonds between carbon and oxygen represents a fractional dipole (arising from the greater electron-attraction of the stronger nucleus,—see the preceding paper), the group as a whole being represented $\overset{\delta+}{\text{—C}}\ \overset{\delta-}{\text{O}_2}\text{—}$; and the processes (*a*) and (*b*) merely transfer electricity from one oxygen atom to the other, leaving unchanged the total negative electrification on the two taken together, and leaving unchanged also the total positive electrification on the carbon atom to which both are attached. Thus the dipole in $\overset{\delta+}{\text{—C}}\ \overset{\delta-}{\text{O}_2}\text{—}$ is two-fold, the smaller separation of charges in C—O being *added* to the larger separation in C=O (compare Part XV), so far as concerns the total charge on the common carbon atom; that is to say, the attachment of ethereal or hydroxylic oxygen should *enhance* the *m*-directing effect of the carbonyl group. Thus the

examination of benzoyl compounds is capable of furnishing definite information as to the type of theory which should be adopted.

The main recorded observations bearing on the point are those of Camps (*Arch. Pharm.*, 1901, **240**, 1), who obtained 55% of *m*-derivative from acetophenone by nitration in nitric acid below 0°, and of Holleman (*Rec. trav. chim.*, 1899, **18**, 267; *Z. physikal. Chem.*, 1899, **31**, 79), who, under similar conditions, obtained 80% of *m*-compound from benzoic acid. Experience of the former reaction has shown the essential correctness of the estimate, and we have closely confirmed Holleman's result for the latter. These facts clearly find their most consistent interpretation in the permanent-strain hypothesis (above), but we have supplemented the evidence thus furnished by a series of experiments designed to determine the relative actions of the groups $-CH_3$, $-NH_2$, $-OH$, $-Cl$ in association with a carbonyl group attached to the benzene nucleus.

According to the conjugative mechanism (above), a series of groups, CR_3, NR_2, OR, Cl, should stand in the same order, as regards their power of competing with phenyl in supplying electrons to the carbonyl group, as they do in regard to their power of furnishing electrons, by an identical mechanism, to a directly attached benzene ring (in $CPhR_3$, $NPhR_2$, etc.), when *op*-substitution results. This order is known and is given by $N>O>Cl>C$, the atom with the most active lone-electrons heading, and that with none terminating, the series. Hence the order of the composite groups should be *

$$\longleftarrow \text{increasing } m\text{-directive power} \longrightarrow$$
$$\cdot CO\cdot CH_3 > CO\cdot Cl > CO\cdot OH > CO\cdot NH_2$$

On the other hand, according to the hypothesis of permanent electron strain, the *m*-directive action should increase with increasing total dipole moment of the group, and this will depend on the disparity in the nuclear attractions exerted on the electrons held in common by two nuclei (Parts XIV and XV). The theoretical sequence is $C\cdot F > C\cdot O > C\cdot N > C\cdot C$; and, on the probable assumption that chlorine will resemble fluorine rather than oxygen, the order of the composite groups should be

$$\longleftarrow \text{increasing } m\text{-directive power} \longrightarrow$$
$$\cdot CO\cdot Cl > \cdot CO\cdot OH > \cdot CO\cdot NH_2 > \cdot CO\cdot CH_3$$

Found (% *meta*-; temp. $-10°$ to $-15°$):

(90%) (82%) (69%) (55%)

* In processes where the mechanism depends upon formal conjugation, such as the activation of the three-carbon system, this is actually the order of the groups (compare Ingold, Shoppee, and Thorpe, J., 1926, 1482).

The numbers in the lower line * represent our results, the last figure being due to Camps, and it will be seen that they give support to the assumptions on the basis of which this sequence is deduced. We have not investigated benzoyl fluoride, but it would probably give a rather higher value than the chloride, and if it were substituted for the chloride in the above table the gaps between the successive members would be still more even than they are at present.

Experimental.

Nitration of Benzoyl Chloride.—The action of nitric acid on benzoyl chloride has been studied by Karslake and Huston (*J. Amer. Chem. Soc.*, 1909, **31**, 479), who used acetic anhydride as the solvent and observed complicated actions during which acetyl as well as nitro-groups entered the nucleus. Preliminary experiments having shown that complete hydrolysis accompanies (and probably precedes) nitration when nitric acid is used both as solvent and as nitrating agent, we operated in our final series with a mixture of nitrogen pentoxide and phosphorus pentoxide in carbon tetrachloride as solvent (compare Part I, J., 1925, **127**, 517). The temperatures ranged from $-10°$ to $-15°$. Due care being taken in the preparation of the nitrogen pentoxide, it is possible under these conditions entirely to avoid hydrolysis, as was shown by evaporating the nitration solution in a slow stream of phosphorus

* It is unnecessary to discuss in detail all the disturbances which might affect the numerical data, because in every case there are reasons either of analogy or of theory for supposing that they would not affect the main result. Thus the figure for acetophenone may be slightly lower than corresponds with the true action of the acetyl group owing to the presence of a small amount of the enol form during nitration; but analogy with the nitration of the nitrobenzophenones (Staedel), where enolisation is impossible, shows that such a disturbance could not be serious; besides, nitration through the enol would lead to the *p*-derivative (Part II, J., 1925, **127**, 873), and actually scarcely any *p*-compound is formed. Some slight additional control might be obtained by the investigation of $\omega\omega'\omega''$-trialkylacetophenones, but we have little doubt that, owing to the polar disturbance of the alkyl groups (as previously illustrated for methyl and ethyl benzoates; J., 1926, 2466), these ketones would give lower, and not higher, meta-values than acetophenone itself. The possible small effects of imidolisation and hydrion addition act in opposite directions as regards the action of the carboxylamide group, and the ionisation of the benzoic acid in the nitric acid solvent would tend to lower the percentage of *m*-isomeride formed (this vol., p. 817, footnote). Even in water, however, the ionisation at a corresponding concentration would only be 0·2%, and it is clear both from an extrapolation of the figures for the benzoic esters (Holleman) and from our experiments on the nitration of benzoic acid in a non-ionising medium ($N_2O_5+CCl_4$) that the disturbance arising from electrolytic dissociation is negligible in comparison with the differences shown in the table above.

pentoxide-dried air, which removes the excess of nitrogen pentoxide and any hydrogen chloride arising from hydrolysis, and then hydrolysing the residue with pure potassium carbonate, when the liberated chloride ion was found to be equivalent to the organic acids to within the limits of experimental error. If the nitrogen pentoxide used is contaminated with its double compound with nitric acid, a certain amount of hydrolysis may occur, but as this appears to make no difference whatever to the proportions of isomerides ultimately found, it is concluded that nitration by nitrogen pentoxide is rapid and that the hydrolysis is subsequent. The separation of the isomeric nitrobenzoic acids was carried out by the methods illustrated in previous papers of this series, which were again checked by application to artificial mixtures. It should, however, be mentioned that the proportion of *p*-isomeride formed in the present instance was smaller than the corresponding solubility correction (2%), so that we can only assign this value as a maximal limit. The values for the *m*-isomeride ranged from 90—91%, except one (Expt. 11; 89%) which is known to be low as a trace of *m*-acid was lost through the " creeping " of the ethereal solution.

(Expt. 3.) Conditions: benzoyl chloride, 2·545 g.; nitrogen pentoxide, 10 g.; carbon tetrachloride, 50 g. containing phosphorus pentoxide in suspension; temperature, — 10°; time allowed for nitration, 2 hours. Results: benzoic acid, by sublimation, nil; *p*-nitrobenzoic acid, less than 2·1%; *m*-nitrobenzoic acid, 90·2%.

The mean (excluding Expt. 11) was 90·3% meta-, the mean temperature being —12·5°.

Nitration of Benzoic Acid.—These experiments need not be described in view of Holleman's previous investigation, and it suffices to state that our value for the proportion of *m*-isomeride formed by nitration at 0° by 10 parts by weight of nitric acid ($d^{16°}$ 1·505) is 80·0%, closely agreeing with Holleman's figure, 80·3%, for the same temperature. The value 81·7%, given in the introduction as 82%, is corrected to correspond with — 12·5° (the approximate mean temperature of the other nitrations) by means of Holleman's correction factor.*

As shown above (p. 839, footnote), the value 82% may be slightly lower than corresponds with the true action of the un-

* In a preliminary experiment on the nitration of benzoyl chloride by excess of fuming nitric acid at +15°, the value 78·6% was obtained for the proportion of *m*-isomeride. This experiment was done before it was realised that hydrolysis precedes nitration under these conditions, but it is now evident that the value agrees with Holleman's figure for the *nitration of benzoic acid* corrected to that temperature (78·3%), and with our own value similarly corrected (78·0%).

ionised carboxyl group, but the other value, namely 85·7%, which we have obtained by nitrating benzoic acid with nitrogen and phosphorus pentoxides in carbon tetrachloride under the conditions used for benzoyl chloride is almost certainly too high, since part of the material will doubtless have been nitrated as benzoic anhydride, which would be expected to give a definitely higher value than the un-ionised acid.

Nitration of Benzamide.—Benzamide was nitrated with excess of fuming nitric acid in the usual way and any nitrobenzoic acids formed by hydrolysis were separated from the neutral amides by means of ether and potassium carbonate. The hydrolysis accompanying nitration was usually of the order of 10%, and the degree of mononitration 97—100%. After analysis, the amides were hydrolysed by boiling for 16 hours with 8% potassium hydroxide solution, preliminary experiments with *m*-nitrobenzamide having shown that hydrolysis is complete and quantitative under these conditions. The nitrobenzoic acids were then separated as usual, any benzoic acid arising from incomplete nitration being previously eliminated by sublimation below 100°. Since it is not known whether the hydrolysis which occurs during nitration is antecedent or subsequent to the entrance of the nitro-group, the acid by-product was also separated into its component isomerides in order to see how each of these two alternative hypotheses would affect the result: actually it makes very little difference which view is adopted. On either hypothesis, the individual values for the proportion of *m*-nitrobenzamide formed all lay between 69 and 70%. The proportions of *p*-derivative being always less than the corresponding solubility correction, we are only able to quote 3% as a maximal limit.

(Expt. 44.) Conditions: benzamide, 2·00 g.; nitric acid ($d^{16°}$ 1·505), 30 g.; temperature, — 15°; time allowed for nitration, 6 hours. Results: hydrolysis, 10%; benzoic acid, nil; *p*-nitrobenzoic acid, less than 3%; *m*-nitrobenzoic acid, 69·6%. This is the proportion of *m*-nitrobenzamide formed if the 10% of hydrolysis entirely precedes nitration. The acid by-product contained 66% of *m*-isomeride, so that if the hydrolysis is wholly subsequent to nitration, the proportion of *m*-nitrobenzamide *formed* would be 69·2%. The mean value 69·4% is regarded as the most trustworthy.

The final mean is the same figure, *viz.*, 69·4% meta-. This, and the other mean figures, are rounded in the table given in the introduction, since it is doubtful if much significance attaches to the decimals.

THE UNIVERSITY, LEEDS. [*Received, December 21st*, 1926.]

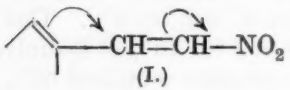
CXXII.—*The Nature of the Alternating Effect in Carbon Chains. Part XVII. The Directive Action of the Groups* $\cdot CH_2 \cdot CH_2 \cdot NO_2$, $\cdot CH{:}CH \cdot NO_2$ *and* $\cdot C(NO_2){:}CHR$ *in Aromatic Substitution.*

By JOHN WILLIAM BAKER and IAN STUART WILSON.

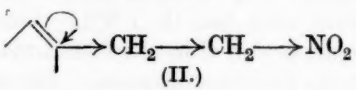
IN preceding parts of this series (Goss, Ingold, and Wilson, J., 1926, 2440; Baker and Ingold, *ibid.*, p. 2462; this vol., p. 261) it is shown that positive poles and the positive ends of dipoles constitute strongly *m*-orienting influences, the effectiveness of which decreases with the intercalation of successive saturated carbon atoms between the charged atom and the nucleus (Goss, Hanhart, and Ingold, this vol., p. 250).

It has been generally assumed that the propagation of electronic disturbances originating in a polar group takes place much more readily in unsaturated carbon chains with conjugated double linkings than in fully saturated carbon chains of similar length, and there is little doubt that this is so in reactions which involve a complete co-valency change such as occurs in triad tautomerism and in the Michael and aldol reactions (Ingold, Shoppee, and Thorpe, J., 1926, 1482; Cooper, Ingold, and Ingold, *ibid.*, p. 1868).

On the other hand, the same view would also be implicit in mechanisms of *m*-substitution in which the conjugation between the nuclear and the side-chain double linking played a fundamental rôle (compare Part XVI), and on the basis of such mechanisms it is to be expected that the transmission of a *m*-orienting influence would be facilitated by the presence of an unbroken conjugated system extending from the polar group throughout the nucleus; thus, on this view, the ω-nitrovinyl group (I) should be more strongly *m*-orienting than the ω-nitroethyl group (II), and so on:



(I.)



(II.)

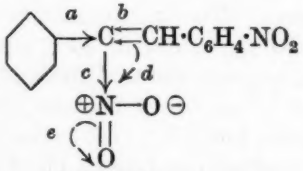
Nevertheless, it may be thought doubtful whether such radical electronic disturbances occur even momentarily in the reactions considered, and whether the conjugation referred to is essential to the process of orientation; a preferable view seems to be (Baker and Ingold, Part XV, this vol., p. 833) that a strain or small shift of average position of the electrons is propagated from the polar group, and that it is the degree of inequality in which the electrons are shared at the junction with the aromatic nucleus which determines the *m*-orienting action of the group. If this be so, then,

although the arrangement and mobility of the electrons in a non-polar double linking are still matters of speculation, the ethylenic bond undoubtedly represents a high degree of unsaturation which must arise from an adjustable electric field at this point, and therefore it is conceivable that the effect due to a positive charge, such as that of the nitro-group in ω-nitrostyrene, will be neutralised during passage through this field, and never reach the nucleus; the true orienting group will then be the α-carbon atom, and the behaviour of the compound to substituting agents should resemble that of toluene (compare Priebs, *Annalen*, 1886, **235**, 347). Toluene, on nitration in nitric acid, gives 3% of *m*-derivative. On the other hand, the hypothesis (Baker and Ingold, Part XI, this vol., p. 261) of the equivalence between the dipoles of a nitro-group and a primary ammonium salt group (Moore's constitution) requires that β-phenylnitroethane should yield the same proportion of *m*-nitro-derivative as does β-phenylethylamine. β-Phenylethylamine, on nitration, gives 12% of *m*-derivative (Goss, Hanhart, and Ingold, Part X, *loc. cit.*). Hence β-phenylnitroethane should, on this theory, yield definitely more than the unsaturated analogue. Experimental evidence, therefore, should enable a decision to be made between the two suggested mechanisms.

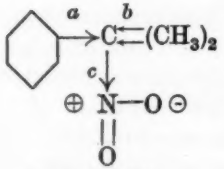
We find that ω-nitrostyrene, on nitration, yields 2% of the *m*-nitro-derivative, whilst β-phenylnitroethane under similar conditions gives 13%.

There is another possible explanation of this result, namely, that the vinyl double bond itself acts as a powerful electron source towards the nucleus, and thus dominates the electron-attraction of the nitro-group. To test this possibility, we have investigated the nitration of an α-nitrovinylbenzene, *viz.*, *p*-nitrobenzylidene-phenylnitromethane (III), in which the double bond is similarly situated with respect to the nucleus but is not in the path of transmission from the nitro-group. In this case, we find more than 20% of *m*-substitution, from which it is clear that the vinyl group, as such, has not a powerful *op*-orienting influence. Indeed, it seems

(III.)



(meta, 21%)



(IV.)

(meta, 29%)

remarkable that the double bond does not compete more effectively with the phenyl group in satisfying the electron-demand of the

nitro-group, until it is remembered that each change (*d*) will be accompanied by a change (*e*) on which it is dependent, and that the two together do not alter the charge on the nitrogen atom. All that competes with the *m*-orienting shift (*a*) in satisfying the electron demand (*c*) of the positive pole is the strain represented by (*b*) (inequality of sharing) and it is therefore not surprising that the effect of a group :CHR in modifying the directive action of a nitromethyl side-chain is not much greater than that of the *gem*-dimethyl group (IV) (Baker and Ingold, Parts IX and XI, *loc. cit.*).

EXPERIMENTAL.

A. *Preparation of Materials.*—*ω-Nitrostyrene* was prepared by Thiele and Haeckel's method (*Annalen*, 1902, **325**, 7).

α-Nitro-β-phenylethane was prepared in accordance with the scheme: $CH_2Ph{\cdot}CH_2{\cdot}OH \xrightarrow{PBr_3} CH_2Ph{\cdot}CH_2Br \xrightarrow{AgNO_2} CH_2Ph{\cdot}CH_2{\cdot}NO_2$. Phosphorus pentabromide in slight excess was added in small, successive portions to β-phenylethyl alcohol, cooled in a freezing mixture. The reaction mixture was finally heated for 0·25 hour on the steam-bath. The product, after cooling, was poured on ice and water, the bromide extracted with ether, and the ethereal solution washed with water and with sodium carbonate solution. The residue from the dried ethereal extract had b. p. 99—103°/14 mm. (compare Grignard, *Compt. rend.*, 1904, **138**, 1049).

A mixture of the bromide and freshly prepared, dry silver nitrite in equal molecular quantities was left in the dark, with frequent shaking, for 1 week. It was then heated at 50—60° for 2 hours, the nitro-compound extracted with ether, the residue from the ether dissolved in dilute sodium hydroxide solution, and the insoluble, unchanged bromide extracted with ether. The nitro-compound was precipitated from the alkaline solution with carbon dioxide, extracted with ether, and the residue from the dried, ethereal extract distilled. *α-Nitro-β-phenylethane* has b. p. 125—135°/1 mm. (Found: * C, 61·4; H, 5·8; N, 10·1. $C_8H_9O_2N$ requires C, 63·5; H, 6·0; N, 9·3%). The yield was very small.

p-*Nitrobenzylidenephenylnitromethane*. To phenylnitromethane (5·6 g.) and *p*-nitrobenzaldehyde (6·0 g.), 1 c.c. of 33% aqueous methylamine was added, and the mixture was warmed on the steam-bath (with addition of a few drops of alcohol if necessary) until solution was complete. After remaining for 24 hours at the ordinary temperature, the now almost solid product was filtered off, washed

* Methane produced during the combustion accounts for the low result for carbon. The gas obtained in the nitrogen determination (Dumas) contained nitrogen 84·1%, combustible gas (chiefly methane) 15·9%.

with a little alcohol, and recrystallised from ethyl acetate containing a little ligroin (b. p. 80—100°), being thus obtained in fine, yellow needles, m. p. 155° (Found: C, 62·0; H, 3·9. $C_{14}H_{10}O_4N_2$ requires C, 62·2; H, 3·7%).

B. *Nitration Conditions and General Procedure.*—Nitration was carried out in every case at —15° to —10°, the compound being added slowly to 8—10 volumes of nitric acid (*d* 1·49), mechanically stirred. The product was isolated in the usual manner, the details varying slightly in individual cases. The proportions of the isomerides present were determined by oxidation with 2% potassium permanganate, either before or after separation of most of the *p*-isomeride in the pure state, and determination of the mixed nitrobenzoic acids produced, by Baker and Ingold's method (*loc. cit.*) or the titration method (Baker, this vol., p. 565).

C. *Details relating to Individual Cases.*—*ω-Nitrostyrene* was nitrated by Priebs (*loc. cit.*), who isolated the *o*- and *p*-derivatives, but could find no *m*-isomeride.

(*Expt.* 11.) The nitrostyrene (10 g.) was added in small successive portions to 75 c.c. of nitric acid (*d* 1·49) at —15° during 2 hours, and after a further 3 hours the partly crystalline product was poured on crushed ice and the precipitated nitro-compounds were filtered off, washed, and dried over phosphorus pentoxide in a vacuum (91·5%). A further 3·8% of nitro-compounds was obtained from the dried ethereal extract of the mother-liquor, from which any acid fraction had been removed (total yield, 95·3%) (Found: C, 49·4; H, 3·4. Calc.: C, 49·5; H, 3·1%).

A portion (3·00 g.) of the total nitration product on oxidation gave nitrobenzoic acids in 91% yield (*M*, by titration, 166·7). These, on separation by the chloroform–barium salt method, yielded 1·96 g. of *p*-nitrobenzoic acid, m. p. 228—230°, mixed m. p. 234—235°, which, with the solubility correction (0·05 g.), corresponds to 67% of this isomeride in the mixture. On conversion of the dissolved acids into their barium salts and concentration of the solution to 30 c.c., no crystallisation ensued. Hence the meta-content must be less than 0·06 g., *i.e.*, less than 2% of the whole mixture. On acidification and extraction with ether, the solution of the barium salts yielded 0·89 g. of *o*-nitrobenzoic acid, m. p. 115—130° (corresponding to 30% of the whole), which, after two crystallisations from chloroform, melted alone at 137°, at 145° when mixed with *o*-nitrobenzoic acid, and at 108—120° when mixed with *m*-nitrobenzoic acid. The composition of the nitration product is therefore *p*- 67%, *m*- <2%, *o*- (by difference) 31% (30% being actually isolated). The proportion of meta-isomeride in the mixture of nitrobenzoic acids obtained by an independent oxidation (yield

81·9%) of this nitration product, determined by the titration method, was 1·9%.

(*Expt.* 12.) The main portion of the *p*-isomeride was isolated from the nitration product (yield 99%) (Found: C, 49·5; H, 3·4%) before oxidation. The nitration product (5·105 g.) on extraction with 100 c.c. of boiling, absolute alcohol left a residue (α) (2·274 g.); the extract deposited 1·449 g. of crystals (β). The mother-liquor was evaporated to dryness (γ) on the steam-bath. The fraction α had m. p. 200° (softening at 190°) and was pure ω*p*-dinitrostyrene. On oxidation, the fraction β gave nitrobenzoic acids in 94% yield (*M*, 167·5), which on separation gave *p*-, m. p. 228°, 0·501 g. (65%); no *m*-; and *o*- (by difference) 35%, of which 31% was actually isolated, m. p. (after crystallisation from chloroform) 144—145°, mixed m. p. 147°. Fraction γ, on oxidation, gave nitrobenzoic acids in 82% yield (*M*, 170), which on separation gave *p*-, m. p. 210—220°, 17·9%; *m*-, m. p. 110—114°, mixed m. p. with *m*- 128—131°, mixed m. p. with *o*- 98—120°, 10·1%; *o*- (by difference) 72%, of which 63% was isolated, m. p. 141°, mixed m. p. 142—145°. The composition of the nitration product is therefore: *p*- = 44·3% (α) + 18·4% (β) + 4·8% (γ) = 67·5%; *m*- = 2·7% (γ); *o*- (by difference) = 29·8%.

α-*Nitro*-β-*phenylethane*. Since only a very small quantity of this substance was available, owing to the difficulty of preparation, the result obtained can only be regarded as approximate. The quantity of *m*-isomeride found is, however, in agreement with that obtained on nitration of the corresponding ammonium salt $CH_2Ph{\cdot}CH_2{\cdot}\overset{+}{N}H_3{\cdot}\overset{-}{X}$ (compare p. 843).

(*Expt.* 21.) The nitro-compound (1·069 g.) was added to 15 c.c. of nitric acid (*d* 1·49) at —15° to —10° during 50 minutes, and after ½ hour the temperature was allowed to rise to —5°, a slight evolution of brown fumes then being observed. The product was poured on crushed ice, and the solution obtained was neutralised partly with 10% aqueous sodium hydroxide and finally with precipitated chalk, and extracted with ether. The yield of neutral nitration product was 78·5% (Found: C, 49·8; H, 4·0. $C_8H_8O_4N_2$ requires C, 49·0; H, 4·2%); acid products amounted to 10·8%. The neutral portion, on oxidation, gave nitrobenzoic acids in 70% yield (*M*, 164) (benzoic acid, by sublimation, 10·5%, which was deducted in calculating the percentages of isomerides present), of which 29·4% consisted of *p*-nitrobenzoic acid, m. p. 224—228°, which crystallised, the remainder being extracted with ether. Separation of a representative sample of the extracted portion in the usual manner showed it to consist of *p*-, m. p. 210—215°, mixed m. p. 220—224°, 32·5%; and

m-, m. p. 123—125°, mixed m. p. 135—137°, 18·9%, whence the composition of the nitration mixture was *p*-, 29·4% + (32·5% of 70·5%) = 52·3%; *m*-, (18·9% of 70·5%) = 13·3%; *o*- (by difference), 34·4%.

p-*Nitrobenzylidenephenylnitromethane.* (*Expt.* 31.) In this, a preliminary experiment, the nitromethane (0·832 g.) was added to 10 c.c. of nitric acid (*d* 1·49) at —20° to —15° during 0·75 hour, the product was left in the freezing mixture for 1·3 hours and then poured on crushed ice, and the precipitated solid (yield 82%) was filtered off, washed, and dried in a vacuum over phosphorus pentoxide (Found: C, 52·9; H, 3·3. $C_{14}H_9O_6N_3$ requires C, 53·3; H, 2·9%). On oxidation, the nitro-compound gave nitrobenzoic acids in 90% yield, a large proportion of the *p*-isomeride being allowed to crystallise before extraction of the mother-liquor with ether. Separation by the chloroform–barium salt method gave, after deduction of the *p*-nitrobenzoic acid produced by oxidation of the *p*-nitrobenzylidene portion of the molecule, *p*-, m. p. 235°, 49%; *m*-, m. p. 125°, mixed m. p. 137—138°, 19·5%; *o*- (by difference), 31·5%.

(*Expt.* 33.) The nitromethane (2·02 g.) gave, under the same conditions as before, 2·306 g. of precipitated nitro-compound (Found: C, 52·6; H, 3·1%) and 0·032 g. extracted with ether (total yield 96%), of which 1·861 g. on oxidation gave 1·081 g. of *p*-isomeride, m. p. 228—232°, mixed m. p. 235°, and 0·540 g. of extracted acids (*M*, by titration, 170) (total yield 83%). On separation, 0·473 g. of the extracted acids gave 0·079 g. of *m*-acid (crystallised), m. p. 131—133°, mixed m. p. 140—141°, and 0·074 g. (extracted), m. p. 124°, mixed m. p. 138° (solubility correction, 0·0054 g.), and 0·077 g. of *p*-nitrobenzoic acid, m. p. 230—232° (solubility correction, 0·007 g.). Hence the composition of the whole of the nitrobenzoic acids obtained (1·620 g.) was *p*-, 1·080 + 0·540/0·473 of (0·077 + 0·007) = 1·175 g.; *m*-, 0·540/0·473 × 0·153 = 0·175 g. Of this 50%, the total yield, 0·810 g. is *p*-nitrobenzoic acid obtained from the oxidation of the *p*-nitrobenzylidene group, so that the 0·810 g. of mixed nitrobenzoic acids obtained by oxidation of the nitrated benzene ring contained *p*-, 0·365 g., and *m*-, 0·175 g., whence the composition is *p*-, 45·1%; *m*-, 21·6%; *o*- (by difference), 33·3%.

(*Expt.* 34.) Under the same conditions as before and by analogous methods of separation, 2·20 g. of the nitromethane yielded 2·542 g. (96%) of neutral nitration product (Found: C, 53·4; H, 2·7%), which, on oxidation, gave nitrobenzoic acids (95% yield) (*M*, 166·8; benzoic acid, by sublimation, 1·6%). Separation as before showed that the composition of the nitrobenzoic acids representing the proportions of isomerides formed by nitration was *p*-, m. p. 233°

either alone or mixed with a pure specimen, 49·7%; *m*-, m. p. 135°, mixed m. p. 141°, 20·9%; *o*- (by difference), 29·4%.

The results obtained are summarised below.

	Percentage of isomerides.					
	By separation.			By titration.	Mean %.	
Substance nitrated.	*o*.	*m*.	*p*.	*m*.	*m*.	*p*.
$CHPh{:}CH{\cdot}NO_2$	31	<2	67	1·9	2	67
	29·8	2·7	67·5			
$CH_2Ph{\cdot}CH_2{\cdot}NO_2$	34·4	13·3	52·3	—	13	52
$CPh(NO_2){:}CH{\cdot}C_6H_4{\cdot}NO_2$	31·5	19·5	49·0		21	48
	33·3	21·6	45·1	—		
	29·4	20·9	47·9			

We desire to thank Professor C. K. Ingold, F.R.S., for his kindly and helpful interest in this investigation, and the Royal Society for defraying part of the expense incurred.

THE UNIVERSITY, LEEDS. [*Received, January 15th*, 1927.]

CXXIII.—*The Determination of Carbonyl in Aldehydes and Ketones.*

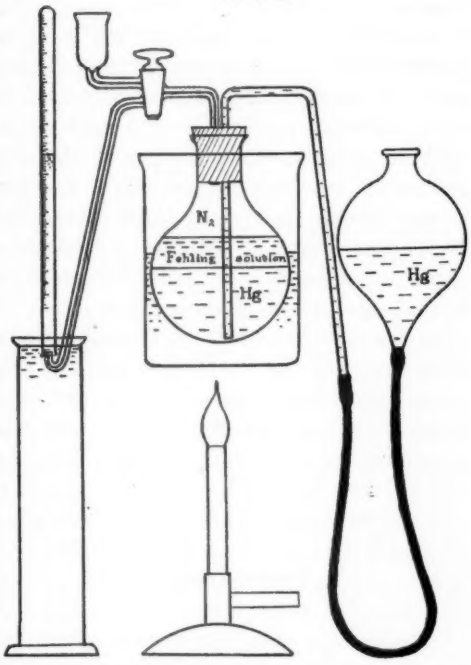
By GEORGE WILLIAM ELLIS.

THE present method is a modification of one described by Strache (*Monatsh.*, 1891, **12**, 514; 1892, **13**, 299). It depends essentially upon the formation of phenylhydrazones and estimation of the excess of phenylhydrazine by measuring the nitrogen evolved by the action of Fehling's solution ($C_6H_5{\cdot}NH{\cdot}NH_2 + O = C_6H_6 + N_2 + H_2O$), a control being carried out upon phenylhydrazine alone. Since the hydrazones do not evolve nitrogen, and since few compounds are likely to interfere with the reaction, the method is of wider application than any other that has been proposed.

Strache used steam to drive out the air from his apparatus and, subsequently, to transfer the evolved nitrogen to the eudiometer, where it was measured saturated with water and benzene vapour. Watson Smith (*Chem. News*, 1906, **93**, 83) substituted carbon dioxide for steam and protected the Fehling's solution by means of a layer of paraffin. Also, to avoid the correction for benzene vapour, the small quantity evolved was nitrated and so absorbed. His apparatus was therefore more elaborate than that of Strache. Both workers recorded satisfactory results, but in the author's experience, both methods are unnecessarily tedious and often untrustworthy. Watson Smith appears to have attributed this to Strache's use of steam, which may cause an evolution of air from the generator or from the water under the eudiometer; but carbon dioxide is required in such quantities as to heat the alkaline solution under the eudio-

meter and thus cause a similar error. Since, however, nitrogen is soluble in water at 100° to the extent of nearly 1% by vol. (Winkler), it will be appreciated that the delay in the cessation of the appearance of nitrogen in the eudiometer is almost entirely due to the solubility of this gas in the solutions employed in the reaction mixture. Strache recommended the use of 200 c.c. of Fehling's solution and about 50 c.c. of the phenylhydrazine solution. Further, the experiments were adjusted so as to yield about 20 c.c. of gas both in the actual estimation and in the control. Hence about 15% of the nitrogen may be retained in solution. This is slowly evolved by the passage of steam through the solutions in Strache's method, but it must be indefinitely retained in the paraffin-protected solutions employed by Watson Smith.

FIG. 1.



The method now described almost entirely obviates the above disadvantages, and utilises the well-known fact that dissolved gases can only be rapidly removed from their solutions by vigorous ebullition under reduced pressure. Further, it is not necessary to arrange for the production of the same volume of nitrogen in the two measurements of each estimation, and thus another possible source of error, due to manipulation of aliquot parts, is avoided.

EXPERIMENTAL.

At the bottom of a strong, short-necked, round-bottomed flask of about 300 c.c. capacity (Fig. 1) are placed about 250 c.c. of mercury, connected with a smaller quantity in a reservoir by means of a glass tube of about 3 mm. bore and rubber tubing. Above the mercury in the flask are placed about 50 c.c. of Fehling's solution. The two-way stopcock connects the upper part of the flask either with a cup of 5—10 c.c. capacity or with the eudiometer, both connexions being

81·9%) of this nitration product, determined by the titration method, was 1·9%.

(*Expt.* 12.) The main portion of the *p*-isomeride was isolated from the nitration product (yield 99%) (Found: C, 49·5; H, 3·4%) before oxidation. The nitration product (5·105 g.) on extraction with 100 c.c. of boiling, absolute alcohol left a residue (α) (2·274 g.); the extract deposited 1·449 g. of crystals (β). The mother-liquor was evaporated to dryness (γ) on the steam-bath. The fraction α had m. p. 200° (softening at 190°) and was pure ω*p*-dinitrostyrene. On oxidation, the fraction β gave nitrobenzoic acids in 94% yield (*M*, 167·5), which on separation gave *p*-, m. p. 228°, 0·501 g. (65%); no *m*-; and *o*- (by difference) 35%, of which 31% was actually isolated, m. p. (after crystallisation from chloroform) 144—145°, mixed m. p. 147°. Fraction γ, on oxidation, gave nitrobenzoic acids in 82% yield (*M*, 170), which on separation gave *p*-, m. p. 210—220°, 17·9%; *m*-, m. p. 110—114°, mixed m. p. with *m*- 128—131°, mixed m. p. with *o*- 98—120°, 10·1%; *o*- (by difference) 72%, of which 63% was isolated, m. p. 141°, mixed m. p. 142—145°. The composition of the nitration product is therefore: *p*- = 44·3% (α) + 18·4% (β) + 4·8% (γ) = 67·5%; *m*- = 2·7% (γ); *o*- (by difference) = 29·8%.

α-*Nitro*-β-*phenylethane*. Since only a very small quantity of this substance was available, owing to the difficulty of preparation, the result obtained can only be regarded as approximate. The quantity of *m*-isomeride found is, however, in agreement with that obtained on nitration of the corresponding ammonium salt $CH_2Ph{\cdot}CH_2{\cdot}\overset{+}{N}H_3{\cdot}\overset{-}{X}$ (compare p. 843).

(*Expt.* 21.) The nitro-compound (1·069 g.) was added to 15 c.c. of nitric acid (*d* 1·49) at —15° to —10° during 50 minutes, and after ½ hour the temperature was allowed to rise to —5°, a slight evolution of brown fumes then being observed. The product was poured on crushed ice, and the solution obtained was neutralised partly with 10% aqueous sodium hydroxide and finally with precipitated chalk, and extracted with ether. The yield of neutral nitration product was 78·5% (Found: C, 49·8; H, 4·0. $C_8H_8O_4N_2$ requires C, 49·0; H, 4·2%); acid products amounted to 10·8%. The neutral portion, on oxidation, gave nitrobenzoic acids in 70% yield (*M*, 164) (benzoic acid, by sublimation, 10·5%, which was deducted in calculating the percentages of isomerides present), of which 29·4% consisted of *p*-nitrobenzoic acid, m. p. 224—228°, which crystallised, the remainder being extracted with ether. Separation of a representative sample of the extracted portion in the usual manner showed it to consist of *p*-, m. p. 210—215°, mixed m. p. 220—224°, 32·5%; and

m-, m. p. 123—125°, mixed m. p. 135—137°, 18·9%, whence the composition of the nitration mixture was *p*-, 29·4% + (32·5% of 70·5%) = 52·3%; *m*-, (18·9% of 70·5%) = 13·3%; *o*- (by difference), 34·4%.

p-*Nitrobenzylidenephenylnitromethane*. (*Expt.* 31.) In this, a preliminary experiment, the nitromethane (0·832 g.) was added to 10 c.c. of nitric acid (*d* 1·49) at —20° to —15° during 0·75 hour, the product was left in the freezing mixture for 1·3 hours and then poured on crushed ice, and the precipitated solid (yield 82%) was filtered off, washed, and dried in a vacuum over phosphorus pentoxide (Found: C, 52·9; H, 3·3. $C_{14}H_9O_6N_3$ requires C, 53·3; H, 2·9%). On oxidation, the nitro-compound gave nitrobenzoic acids in 90% yield, a large proportion of the *p*-isomeride being allowed to crystallise before extraction of the mother-liquor with ether. Separation by the chloroform–barium salt method gave, after deduction of the *p*-nitrobenzoic acid produced by oxidation of the *p*-nitrobenzylidene portion of the molecule, *p*-, m. p. 235°, 49%; *m*-, m. p. 125°, mixed m. p. 137—138°, 19·5%; *o*- (by difference), 31·5%.

(*Expt.* 33.) The nitromethane (2·02 g.) gave, under the same conditions as before, 2·306 g. of precipitated nitro-compound (Found: C, 52·6; H, 3·1%) and 0·032 g. extracted with ether (total yield 96%), of which 1·861 g. on oxidation gave 1·081 g. of *p*-isomeride, m. p. 228—232°, mixed m. p. 235°, and 0·540 g. of extracted acids (*M*, by titration, 170) (total yield 83%). On separation, 0·473 g. of the extracted acids gave 0·079 g. of *m*-acid (crystallised), m. p. 131—133°, mixed m. p. 140—141°, and 0·074 g. (extracted), m. p. 124°, mixed m. p. 138° (solubility correction, 0·0054 g.), and 0·077 g. of *p*-nitrobenzoic acid, m. p. 230—232° (solubility correction, 0·007 g.). Hence the composition of the whole of the nitrobenzoic acids obtained (1·620 g.) was *p*-, 1·080 + 0·540/0·473 of (0·077 + 0·007) = 1·175 g.; *m*-, 0·540/0·473 × 0·153 = 0·175 g. Of this 50%, the total yield, 0·810 g. is *p*-nitrobenzoic acid obtained from the oxidation of the *p*-nitrobenzylidene group, so that the 0·810 g. of mixed nitrobenzoic acids obtained by oxidation of the nitrated benzene ring contained *p*-, 0·365 g., and *m*-, 0·175 g., whence the composition is *p*-, 45·1%; *m*-, 21·6%; *o*- (by difference), 33·3%.

(*Expt.* 34.) Under the same conditions as before and by analogous methods of separation, 2·20 g. of the nitromethane yielded 2·542 g. (96%) of neutral nitration product (Found: C, 53·4; H, 2·7%), which, on oxidation, gave nitrobenzoic acids (95% yield) (*M*, 166·8; benzoic acid, by sublimation, 1·6%). Separation as before showed that the composition of the nitrobenzoic acids representing the proportions of isomerides formed by nitration was *p*-, m. p. 233°

either alone or mixed with a pure specimen, 49·7%; *m*-, m. p. 135°, mixed m. p. 141°, 20·9%; *o*- (by difference), 29·4%.

The results obtained are summarised below.

Substance nitrated.	Percentage of isomerides. By separation. *o*.	*m*.	*p*.	By titration. *m*.	Mean %. *m*.	*p*.
$CHPh:CH\cdot NO_2$	31	<2	67	1·9	2	67
	29·8	2·7	67·5			
$CH_2Ph\cdot CH_2\cdot NO_2$	34·4	13·3	52·3	—	13	52
$CPh(NO_2):CH\cdot C_6H_4\cdot NO_2$	31·5	19·5	49·0	—	21	48
	33·3	21·6	45·1			
	29·4	20·9	47·9			

We desire to thank Professor C. K. Ingold, F.R.S., for his kindly and helpful interest in this investigation, and the Royal Society for defraying part of the expense incurred.

THE UNIVERSITY, LEEDS. [*Received, January 15th*, 1927.]

CXXIII.—*The Determination of Carbonyl in Aldehydes and Ketones.*

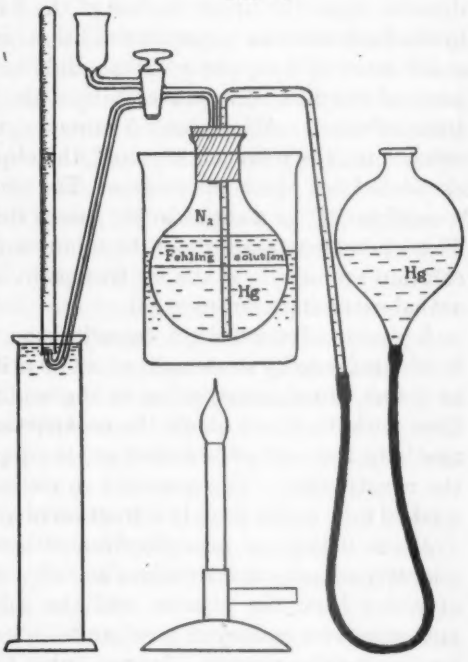
By GEORGE WILLIAM ELLIS.

THE present method is a modification of one described by Strache (*Monatsh.*, 1891, **12**, 514; 1892, **13**, 299). It depends essentially upon the formation of phenylhydrazones and estimation of the excess of phenylhydrazine by measuring the nitrogen evolved by the action of Fehling's solution ($C_6H_5\cdot NH\cdot NH_2 + O = C_6H_6 + N_2 + H_2O$), a control being carried out upon phenylhydrazine alone. Since the hydrazones do not evolve nitrogen, and since few compounds are likely to interfere with the reaction, the method is of wider application than any other that has been proposed.

Strache used steam to drive out the air from his apparatus and, subsequently, to transfer the evolved nitrogen to the eudiometer, where it was measured saturated with water and benzene vapour. Watson Smith (*Chem. News*, 1906, **93**, 83) substituted carbon dioxide for steam and protected the Fehling's solution by means of a layer of paraffin. Also, to avoid the correction for benzene vapour, the small quantity evolved was nitrated and so absorbed. His apparatus was therefore more elaborate than that of Strache. Both workers recorded satisfactory results, but in the author's experience, both methods are unnecessarily tedious and often untrustworthy. Watson Smith appears to have attributed this to Strache's use of steam, which may cause an evolution of air from the generator or from the water under the eudiometer; but carbon dioxide is required in such quantities as to heat the alkaline solution under the eudio-

meter and thus cause a similar error. Since, however, nitrogen is soluble in water at 100° to the extent of nearly 1% by vol. (Winkler), it will be appreciated that the delay in the cessation of the appearance of nitrogen in the eudiometer is almost entirely due to the solubility of this gas in the solutions employed in the reaction mixture. Strache recommended the use of 200 c.c. of Fehling's solution and about 50 c.c. of the phenylhydrazine solution. Further, the experiments were adjusted so as to yield about 20 c.c. of gas both in the actual estimation and in the control. Hence about 15% of the nitrogen may be retained in solution. This is slowly evolved by the passage of steam through the solutions in Strache's method, but it must be indefinitely retained in the paraffin-protected solutions employed by Watson Smith.

FIG. 1.



The method now described almost entirely obviates the above disadvantages, and utilises the well-known fact that dissolved gases can only be rapidly removed from their solutions by vigorous ebullition under reduced pressure. Further, it is not necessary to arrange for the production of the same volume of nitrogen in the two measurements of each estimation, and thus another possible source of error, due to manipulation of aliquot parts, is avoided.

EXPERIMENTAL.

At the bottom of a strong, short-necked, round-bottomed flask of about 300 c.c. capacity (Fig. 1) are placed about 250 c.c. of mercury, connected with a smaller quantity in a reservoir by means of a glass tube of about 3 mm. bore and rubber tubing. Above the mercury in the flask are placed about 50 c.c. of Fehling's solution. The two-way stopcock connects the upper part of the flask either with a cup of 5—10 c.c. capacity or with the eudiometer, both connexions being

of capillary tubing. The flask is almost completely surrounded by a beaker, but only a little boiling water is contained in the latter.

The Fehling's solution must first be freed from dissolved gases. The water in the beaker is kept rapidly boiling, the stopcock is closed, and the mercury reservoir is lowered as far as possible so as to reduce the pressure in the flask. When most of the mercury in the flask has been forced into the reservoir by the vapour formed, the rubber tubing is pinched by a clip and a fine jet of cold water is directed upon the upper surface of the flask. The reduced pressure in the flask causes a vigorous ebullition, and by maintaining as great a difference of temperature as possible between the upper and lower parts of the flask, the greater part of the dissolved gases is removed from solution. After about 5 minutes' constant attention to these conditions, the reservoir is raised, the clip is removed, and the gases are forced out of the apparatus. The process is repeated until only a small break, or a slight froth, passes through the capillary tubing. This operation takes about 15 minutes if only 50 c.c. of Fehling's solution are used. A similar treatment is applied at the end of the actual estimations of nitrogen.

A pipette of about 2 c.c. capacity was constructed from tubing of 5—6 mm. bore by drawing it to a fine orifice at one end and melting to a fine, short constriction in the middle. When this pipette is filled with fluid just above the constriction and held with the outlet touching the wall of a container, the liquid automatically stops at the constriction. The quantity so retained, after being blown and washed out, varies to only a fraction of a mg.

About 0·43 g. of phenylhydrazine hydrochloride, with a similar quantity of anhydrous sodium acetate, was dissolved in 3 measures of water from the pipette, and the solution filtered. Of this, 2 measures were conveyed to separate tubes, the third being employed for rinsing the pipette. In one tube, having a thickened bottom, was broken a small bulb containing 0·0619 g. of salicylaldehyde. Both tubes were placed in a water-bath for a few minutes.

The contents of the tube which held the reagent only were placed in the cup of the apparatus and drawn into the flask by careful lowering of the reservoir. The tube and cup were washed several times, and the washings drawn in, the whole of the phenylhydrazine being thus brought to the top of the Fehling's solution. The reservoir was then lowered until vapour formed at the top of the flask, thereby causing a mixing of the reagents and an evolution of nitrogen and benzene vapour. It may be noted here that an alcoholic solution of the hydrazine base may be employed and that some care must be exercised at this stage, for an injudicious lowering of the reservoir may produce so much vapour as to force the Fehling's

solution out of the flask. In the actual experiment described, the greater part of the mercury was allowed to pass into the reservoir, and the water in the beaker was kept boiling for 3 or 4 minutes, after which most of the nitrogen was transferred to the eudiometer. The remainder of the nitrogen, which was chiefly in solution in the reaction mixture, was removed as described above for the preliminary operation; 20·0 c.c. at 16° and 773·7 mm. were obtained, measured saturated with aqueous and benzene vapours as recommended by Strache.

The excess of phenylhydrazine remaining in the other tube was then estimated. It was necessary to filter off the hydrazone so as to prevent clogging of the capillary; this was effected by means of a small drawn-out tube, plugged with cotton wool and leading into another tube placed in a vacuum filtering-flask. It was thus possible to filter and wash the hydrazone so that the total bulk of liquid was no more than that used in the first estimation. The excess of the reagent, under exactly the same conditions, yielded 9·3 c.c. (Found: CO, 22·2. Calc.: CO, 22·9%).

The results of various estimations by the new method are given below. For those in which more than 0·1 g. of material was taken, 200 c.c. of Fehling's solution were employed, as used by Strache; but the author's method of using smaller quantities was found to be more rapid and even more accurate. The substances taken were carefully purified for the purpose, but their degree of purity was not ascertained.

Results.—Salicylaldehyde; found: CO, 22·2, 24·8, 23·2; calc., 22·9%. Acetone; found: CO, 47·3; calc., 48·2%. Phenylhydrazine; found, 102, 100·1%. Phenylhydrazine hydrochloride; found, 99, 102%.

St. Mary's Hospital,
London, W. 2.

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CXXIV.—*Heterocyclic Compounds containing Arsenic. Part I. The Action of Chloroacetamide on* 3 : 4-*Diaminophenylarsinic Acid.*

By Arthur James Ewins, George Newbery, and Ralph William Ewart Stickings.

In the course of investigations in connexion with the chemotherapy of organic arsenical derivatives, our attention was recently directed to a communication by Lewis and Bent (*J. Amer. Chem. Soc.*, 1926, **48**, 949) in which the action of chloroacetamide on 3 : 4-diaminophenylarsinic acid (I) is discussed. These authors consider

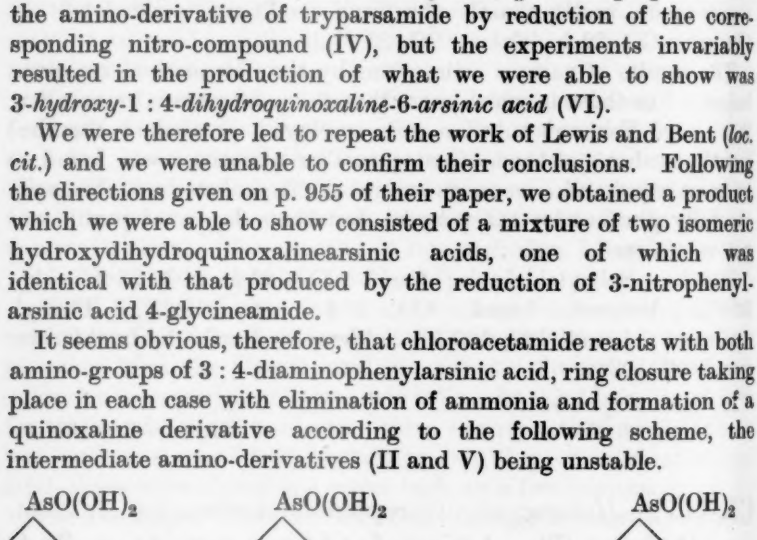
that under their conditions of experiment chloroacetamide reacts preferentially with one amino-group with the production of 3-aminophenylarsinic acid 4-glycineamide (V). They state also that, if the reaction be not carefully controlled, ring closure takes place with elimination of water and the formation of a quinoxaline derivative, $(HO)_2OAs{\cdot}C_6H_3{<}\begin{matrix}N{=}C{\cdot}NH_2\\ NH{\cdot}CH_2\end{matrix}$, the reaction being analogous to the formation of a phenylquinoxaline from ω-bromoacetophenone and *o*-phenylenediamine (Fischer and Romer, *Ber.*, 1908, **41**, 2350). The reaction is suggested as a new method of preparing quinoxalines containing an amino-group.

The production of 3-aminophenylarsinic acid 4-glycineamide is of interest, as this compound is a derivative of tryparsamide, phenylarsinic acid 4-glycineamide, which is a product of considerable therapeutic value.

One of us (R. W. E. S.) had already attempted the preparation of the amino-derivative of tryparsamide by reduction of the corresponding nitro-compound (IV), but the experiments invariably resulted in the production of what we were able to show was 3-*hydroxy*-1 : 4-*dihydroquinoxaline*-6-*arsinic acid* (VI).

We were therefore led to repeat the work of Lewis and Bent (*loc. cit.*) and we were unable to confirm their conclusions. Following the directions given on p. 955 of their paper, we obtained a product which we were able to show consisted of a mixture of two isomeric hydroxydihydroquinoxalinearsinic acids, one of which was identical with that produced by the reduction of 3-nitrophenylarsinic acid 4-glycineamide.

It seems obvious, therefore, that chloroacetamide reacts with both amino-groups of 3 : 4-diaminophenylarsinic acid, ring closure taking place in each case with elimination of ammonia and formation of a quinoxaline derivative according to the following scheme, the intermediate amino-derivatives (II and V) being unstable.



The formation of these quinoxalines has been confirmed by analysis. Lewis and Bent apparently only determined the percentage of arsenic in their product. Determination of nitrogen would have undoubtedly shown them the true nature of the compound produced.

The constitution of 3-hydroxy-1 : 4-dihydroquinoxalinearsinic acid (VI) is established by its identity with the product obtained by reduction of 3-nitrophenylarsinic acid 4-glycineamide (IV). It is therefore highly probable that (III) has the constitution denoted, and experiments are in progress to establish this by synthetic methods also.

EXPERIMENTAL.

Action of Chloroacetamide on 3 : 4-Diaminophenylarsinic Acid.—Following the procedure outlined by Lewis and Bent (*loc. cit.*), 25 g. of 3 : 4-diaminophenylarsinic acid were dissolved in a solution of 4·1 g. of sodium hydroxide in 105 c.c. of water, 19·4 g. of chloroacetamide were added, and the mixture was boiled under reflux for 45 minutes. Concentrated hydrochloric acid (7·8 c.c.) was added to the cooled solution. A crystalline solid readily separdate which was seen under the microscope to consist of a mixture of long, fine needles and tetrahedra. The product was in part somewhat readily soluble in hot water, completely soluble in dilute alkali solution, and insoluble in dilute mineral acids. Treatment with caustic soda solution produced only a trace of ammonia. The crude product was purified by reprecipitation from dilute sodium carbonate solution after treatment with charcoal (yield, 15 g.) (Found : As, 27·5; N, 10·5. $C_8H_9O_4N_2As$ requires As, 27·6; N, 10·3%).

Separation of the Isomeric Quinoxalines.—The product (12 g.) was boiled with successive quantities (50, 25, 25, 25 c.c.) of water, the hot extracts were combined, and the crystalline product obtained on cooling was repeatedly crystallised from water, being finally obtained in long, nearly white, prismatic needles, which did not decompose at 260°. Analysis indicated it to be *3-hydroxy-1 : 4-dihydroquinoxaline-6-arsinic acid* (VI) (Found : As, 27·4; N, 10·35%).

A *monobenzoyl* derivative was obtained by the Schotten–Baumann method. It crystallised from 50% alcohol, in which it was readily soluble, in lustrous, hexagonal plates, which did not decompose below 290° (Found : As, 19·85; N, 7·45. $C_{15}H_{13}O_5N_2As$ requires As, 20·0; N, 7·4%).

3-Hydroxy-1 : 4-dihydroquinoxaline-6-arsinic acid was readily obtained again on boiling the monobenzoyl derivative with 5% sodium hydroxide solution for 15 minutes.

2-Hydroxy-1 : 4-dihydroquinoxaline-6-arsinic acid (III) was ob-

tained by purification of the less soluble fraction (about 6·8 g.) left after extraction of the original mixture with hot water. Owing to the general insolubility of the compound in neutral solvents, purification was effected by means of the sodium salt. The acid was dissolved in just sufficient sodium carbonate solution to produce a neutral or faintly alkaline solution. To the hot filtered solution alcohol was added gradually until crystallisation of the sodium salt commenced. On standing, a semi-solid crystalline mass of needles was obtained. The crystals were filtered off, washed with a little alcohol, and dissolved in hot water, and the hot solution was made just acid to Congo-red. On standing, the *acid* separated in diamond-shaped plates, m. p. 258° (decomp.) (Found: As, 27·7; N, 10·4%).

A *monobenzoyl* derivative was obtained in the usual way. The alkaline reaction product was made just acid to Congo-red with dilute hydrochloric acid, and the precipitated benzoic acid removed in ether. The aqueous solution slowly deposited the *benzoyl* derivative, which crystallised from water in stout, hexagonal plates, m. p. 251—252° (Found: As, 20·1; N, 7·8%).

Nitration of Phenylarsinic Acid 4-Glycineamide.—A solution of 220 g. of the sodium salt of phenylarsinic acid 4-glycineamide in 800 c.c. of concentrated sulphuric acid was cooled to 0° and slowly treated with a mixture of 46 c.c. of nitric acid (*d* 1·42) and 46 c.c. of concentrated sulphuric acid, the temperature being maintained below 5°. After being kept for 30 minutes, the reaction mixture was poured on 1 kg. of ice, 4 litres of water were added, and the whole was stirred; crystallisation then started. After cooling to 0°, the crystals were filtered off, washed free from mineral acid, and dried. The product was an intensely yellow, crystalline substance (yield, 155 g.) soluble in alkalis to a dark red solution (Found: As, 23·4; N, 13·2. $C_8H_{10}O_6N_3As$ requires As, 23·5; N, 13·2%).

Reduction of 3-Nitrophenylarsinic Acid 4-Glycineamide with Ferrous Hydroxide. Production of 3-Hydroxy-1:4-dihydroquinoxaline-6-arsinic Acid.—3-Nitrophenylarsinic acid 4-glycineamide (100 g.) was dissolved in 800 c.c. of saturated sodium carbonate solution, and added to a cooled precipitate of alkaline ferrous hydroxide produced by pouring a solution of 300 g. of caustic soda in 400 c.c. of water into a cooled solution of 800 g. of ferrous sulphate in 800 c.c. of water. The temperature of the reduction was maintained at 30° for 1 hour, with occasional stirring, during which a strong smell of ammonia was noticed. The reaction mixture was then filtered, and the yellow filtrate was acidified to Congo-paper by addition of 50% sulphuric acid, crystallisation commencing immediately. After 10 minutes, the crystals were filtered off, washed, and purified by solution in dilute aqueous sodium

carbonate and reprecipitation with excess of mineral acid. The product so obtained was a yellowish-white, crystalline substance, soluble in alkalis and insoluble in mineral acids. No ammonia was evolved on warming it with excess of caustic soda solution. It was moderately easily soluble in boiling water, from which it crystallised in long, prismatic needles which did not decompose below 260° (yield, 45 g.) (Found: As, 27·5; N, 10·4. Calc. for $C_8H_9O_4N_2As$: As, 27·5; N, 10·3%). This substance was identified with the compound (VI) by its crystalline form, solubility, and analysis and also by comparison of the monobenzoyl derivatives.

RESEARCH LABORATORY, MESSRS. MAY AND BAKER, LTD.,
WANDSWORTH, S.W. 18. [*Received, January 21st*, 1927.]

CXXV.—*The Properties of Malonic Anhydride* (*Carbon Suboxide*), C_3O_2.

By MORRIS J. EDWARDS and JOHN M. WILLIAMS.

A QUANTITY of carbon suboxide has been prepared by the method of Diels and Meyerheim (*Ber.*, 1907, **40**, 359) with a view to the study of the kinetics of its process of polymerisation in the gaseous state. Also, since it was a comparatively simple matter to prepare the oxide in the pure state, the vapour pressure was measured over the range — 62° to 4°.

The oxide in the gaseous state proved to be very stable, even at room temperature, when dry and contained in a glass vessel the surface of which had not been previously contaminated with the polymerised product. On the other hand, it could not be stored over mercury for any length of time, or in the presence of moisture without polymerisation occurring. The dried gas is not appreciably affected by insolation with ultra-violet light.

The polymerisation occurs on the surface of the containing vessel, and from the measurement of the velocity of chemical change, the process is seen to be very complex.

EXPERIMENTAL.

The method of Diels and Meyerheim was adopted with slight modifications. Mixtures of 20 g. of pure malonic acid and 200 g. of powdered phosphorus pentoxide were placed in a 350 c.c. flask of hard glass and, after evacuation by means of a Langmuir pump, heated by suddenly plunging the flask into an oil-bath at 140—

160°. The gases liberated were withdrawn as rapidly as possible from the hot flask and cooled by passage through tubes immersed in a freezing mixture of ice and salt, and in liquid air. A mixture of acetic acid, carbon dioxide and carbon suboxide condensed in the tube immersed in liquid air. The temperature of the mixture was allowed to rise slowly and the bulk of the carbon dioxide evaporated into the air. When a temperature of 7° was reached, the gas was collected in a mercury reservoir; the first fraction was rejected, as it was contaminated with much carbon dioxide, and the second fraction was condensed as rapidly as possible in a 3 c.c. bulb immersed in liquid air. The liquid carbon suboxide was freed from carbon dioxide at −50° by connecting the bulb repeatedly with an evacuated space (10 c.c.) until the liquid gave a constant vapour pressure. The purity of the preparation was shown by the vapour density, which was 34·3.

Determinations of Vapour Pressure at Various Temperatures.—About 2 c.c. of carbon suboxide were condensed in a small bulb, to which was attached a mercury manometer by a glass-to-glass connexion. Since the suboxide slowly polymerises on the surface of mercury, the manometer was shut off by a tap except when measurements were being taken. Vapour-pressure determinations were made between −62° and 4°, in a bath of alcohol contained in a Dewar vessel as a thermostat. The alcohol was cooled by means of solid carbon dioxide. After every reading the bulb was placed in liquid air, and the vapour-pressure readings showed that no appreciable decomposition occurred throughout the experiments. In the table are given the readings of the manometer. Those at −62° are the successive values obtained during the removal of carbon dioxide.

Vapour Pressure Readings.

Temp.	−62°	−62°	−62°	−62°	−62°
Vap. press. (cm.)	5·80	3·55	2·85	2·45	2·30
Temp.	−62°	−62°	−52°	−44°	−39°
Vap. press. (cm.)	2·30	2·30	3·83	6·48	8·67
Temp.	−35°	−31°	−27°	−24°	−21°
Vap. press. (cm.)	10·97	13·61	16·69	19·34	22·37
Temp.	−16°	−11°	−6°	0°	+4°
Vap. press. (cm.)	28·47	35·97	44·62	57·52	67·32

From the vapour pressure curve, the boiling point at atmospheric pressure is 6·8°.

The heat of vaporisation was calculated from the above data by means of the expression $d \log p/dT = -Q/RT^2$, and the values for the range of temperature −62° to 4° are given below.

Values of Q for the Different Temperature Ranges.

Range ...	−62° to −52°	−52° to −44°	−44° to −39°	−39° to −35°
Q (Cal.) ...	4·74	6·62	6·16	6·57
Range ...	−35° to −31°	−31° to −27°	−27° to −24°	−24° to −21°
Q (Cal.) ...	6·18	6·03	6·02	6·06
Range ...	−21° to −16°	−16° to −11°	−11° to − 6°	− 6° to 0°
Q (Cal.) ...	6·22	6·27	6·00	6·14
Range ...	0° to 4°			
Q (Cal.) ...	5·93			

The mean value of Q between −31° and 4° is 6·08 Cal.

Velocity of Chemical Change.—Purified liquid carbon suboxide was vaporised into a glass bulb of 80 c.c. capacity. The bulb had been used previously in an experiment in which a red film of polymerised product had been deposited. This was removed by means of water and chromic acid. The polymerisation was accompanied by a decrease in pressure. The pressure was observed at constant volume and temperature (12°). The following readings were obtained for an initial gas pressure of 44·39 cm.

Time (hrs.)	0·25	0·75	1·75	2·75	4·75	6·75
Change of press. (cm.) ...	0·55	2·90	3·86	4·08	4·25	4·50

The values of the velocity coefficient, k, calculated from the above data, on the assumption that from 1 to 6 molecules may be taking part in the change, fall off with time. The reaction is probably a catalytic surface reaction. The fact that the speed of the reaction falls off with time may be explained by the fact that the vapour must diffuse through the layer of decomposed or polymerised product to the surface of the glass before it can undergo change.

Our thanks are due to Mr. W. E. Garner for his helpful advice and the interest which he took in the work.

THE SIR WILLIAM RAMSAY PHYSICAL AND INORGANIC LABORATORIES, UNIVERSITY COLLEGE, LONDON. [*Received, February 3rd*, 1927.]

CXXVI.—*The Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. Part II.*

By ROBERT WINSTANLEY LUNT and RAMAVENKATASUBBIER VENKATESWARAN.

In the first communication of this series (J., 1925, **127**, 2052) an account was given of the decomposition of a fixed amount of carbon monoxide, enclosed in the annular space of a Siemens ozoniser,

when subjected to ionisation by collision produced by alternating electric fields of frequency 250 cycles per sec. The decomposition was accompanied by the formation of a brown solid on the walls of the ozoniser, and equilibrium was attained when the residual gas contained 1 part of carbon dioxide to approximately 12 parts of the monoxide. Those experiments showed also that the composition of the brown solid, which was calculated from the results of analysis of the residual gases at equilibrium, varied with the initial pressure of the carbon monoxide, the ratio of carbon to oxygen increasing as the initial pressure of the monoxide diminished. In addition, it was found that the composition of the solid was independent of the potential applied to the ozoniser electrodes in the range examined, *viz.*, 4000—9000 volts.

Further experiments at the same frequency have now been carried out with the aim of more completely elucidating the nature of this substance. The apparatus has been modified in order to produce relatively large amounts, of the order of several grams, and to ensure that the "suboxide" should be formed at a constant partial pressure of the monoxide and in the absence of appreciable quantities of the dioxide. The conditions of formation are therefore more exactly defined than in the earlier experiments in which the carbon dioxide produced was not removed. Despite the improved technique, the preparation of the suboxide in quantity is a slow process, and is rendered difficult by a tendency to decompose spontaneously in air.

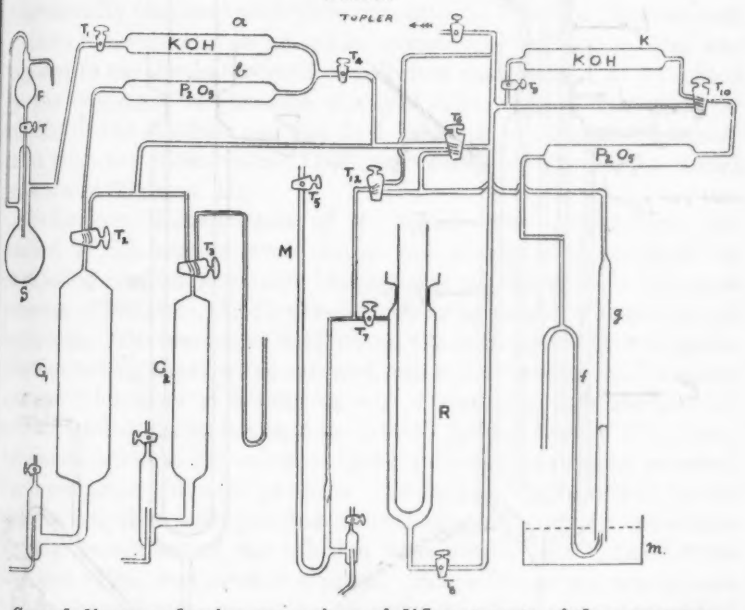
Experimental.

The electrical technique employed was identical with that described in Part I of this series.

Reaction Vessel.—The vessel which contained the gas while it was subjected to the discharge (Fig. 2) was that employed previously, *viz.*, a Siemens ozoniser constructed of glass, and connected to the auxiliary apparatus as represented in Fig. 1. The inner tube, t_1, was ground to fit the outer tube, t_2, at one end, thus facilitating the removal of any substance formed in the annular space between the tubes. It was filled with mercury, which served as the high-tension electrode, E_1. A glass tube containing mercury surrounded the outer tube and formed the low-tension electrode, E_2, which was earthed. The electrodes were water-cooled and their temperatures were recorded by alcohol thermometers. The external diameters of the two tubes of the reaction vessel were 25·5 and 15·2 mm., respectively, and the internal diameters were 23·3 and 12·7 mm., the thicknesses being thus 1·1 and 1·25 mm., respectively. The total volume included between the stopcocks was 81 c.c., and the effective length of the electrode was 33 cm.

An automatic Sprengel pump, *fg*, circulated the gas continuously through the discharge. The gas was led from the reaction vessel by the tap, T_8, through some 6 feet of tubing containing caustic potash, *K*, and then over phosphorus pentoxide to the fall tube, *g*, of the Sprengel pump. From the pump the gas flowed to the reaction vessel *via* the taps T_{12} and T_7. The circulating system was connected by the taps T_{12} and T_6 to gas holders containing the monoxide, G_1G_2, in such a manner that this could be fed in as rapidly as the dioxide was removed by the potash. In this way an approximately constant pressure was maintained in the gas sub-

FIG. 1.



General diagram showing connexions of different parts of the apparatus.

jected to the discharge. A mercury manometer, *M*, was attached to the system as before.

Preparation of Carbon Monoxide.—The gas was produced free from oxygen by the method described previously, in which recrystallised formic acid contained in the bulb, *F*, was allowed to drop into an evacuated flask, *S*, containing warm concentrated sulphuric acid.

Procedure.—In order to facilitate the rapid formation of the suboxide, the highest available potential was employed in all experiments, *viz.*, 10,000 volts r.m.s.; the corresponding current varied slightly with the pressure from 9—10 milliamps.

The method adopted for preparing quantities of about 2 g. of the suboxide consisted in circulating carbon monoxide continuously through the reaction vessel until about 5 litres had been consumed, the potash tube for absorbing carbon dioxide being connected in the circulating system. The supply of monoxide was adjusted to

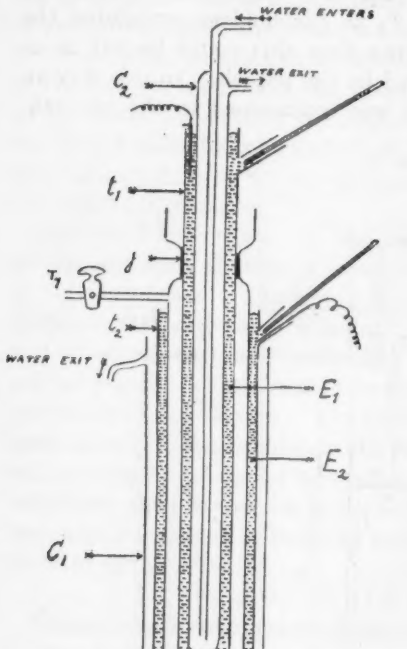


FIG. 2.

Reaction vessel.

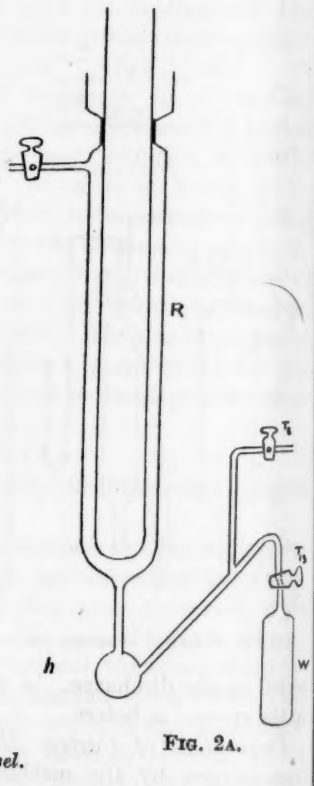


FIG. 2A.

maintain the pressure constant within $\pm$ 5 mm. Hg. After the discharge was stopped, the reaction vessel was disconnected from the circulating system and filled with dry air. The inner tube was then removed from the outer tube, and the suboxide scraped off as rapidly as possible on account of its very hygroscopic nature and transferred to a vacuum desiccator containing phosphorus pentoxide. As soon as the inner tube had been withdrawn, the grease was

removed from the ground joint of the outer tube, which was then filled with pure dry ether, and the solid adhering to the walls was loosened by rubbing with a clean dry copper rod. The ether and the solid were transferred to a flask and the former was removed by distillation, the residue being placed in a vacuum desiccator to remove the last traces of ether. The ether which had been in contact with the solid was not coloured, and on evaporation to dryness left no residue. The brown solid is therefore insoluble in ether, the use of which, to protect the solid from atmospheric contamination, would appear to be permissible.

In order to ascertain whether the conditions of experiment were substantially identical with those described in Part I, a fixed amount of carbon monoxide, at an initial pressure of 528·4 mm. Hg, was exposed to the discharge until equilibrium was reached, as indicated by the cessation of pressure change. The ratio of monoxide to dioxide in the residual gas was 11·4, which is in satisfactory agreement with the mean value, 11·58, previously obtained at an initial pressure of 501 mm. Hg.

Preliminary Examination of the Solid.—The experiments described in this section were carried out on the solid prepared by circulating carbon monoxide through the discharge at a constant pressure of 500 mm., the dioxide formed being removed continuously by potash. On treatment with water, the solid gave a brown, acidic solution having the smell of caramel, and a dark brown residue which was insoluble even in boiling water. Titration of this solution by standard alkali indicated that its acidity did not change with time. An examination of the solution under the ultramicroscope revealed the presence of colloidal particles. Prolonged boiling of the brown aqueous solution with purified animal charcoal did not decolorise it. The treatment of the solution with purified norit, freed from lime and silica, was more successful. Some five or six treatments with fresh norit were necessary, however, to give a nearly colourless solution. It was extremely tedious to prepare a colourless solution. The nitrates of aluminium, sodium, and thorium were also effective in partly decolorising the solution. Dialysis through a collodion membrane, although satisfactory in other ways, was too slow to be serviceable. The nearly colourless solution of the suboxide obtained by any of these methods was acid to litmus and reduced acidified potassium permanganate solution. When neutralised with ammonia the solution gave with calcium chloride a white, crystalline precipitate insoluble in acetic acid, and a white precipitate with silver nitrate, indicating that the original solution contained oxalic acid.

On concentrating the nearly decolorised solution of the brown solid obtained by treatment with norit, colourless crystals were

obtained, m. p. 96—100° (m. p. of hydrated oxalic acid, 100°). Similar crystals were obtained by extracting with dry ether, in a Soxhlet apparatus, the solid remaining when the brown aqueous solution of the suboxide was evaporated to dryness. After recrystallisation from dry ether, colourless crystals were obtained which, alone or when mixed with pure hydrated oxalic acid, melted at 98—99°. The crystals were compared microscopically with those of oxalic, malonic, and succinic acids, and found to be very similar to the first. The *p*-toluidine derivative, after recrystallisation from absolute alcohol, had m. p. 265—266° (oxalo-*p*-toluidide melts at 266—267°).

The silver or calcium salt precipitated from the neutralised, nearly colourless solution of the brown solid carried with it the residual colouring matter in the solution. The silver salt thus obtained could not therefore be used to determine accurately the equivalent of the acid. It would appear, however, that ignition of the calcium salt leads to values for the oxalic acid content of the solution, but such data are reserved for a later communication. The equivalent of the acid has, however, been determined by igniting the silver salt, dried at 100°, obtained from two different dialyses of a solution of the brown solid through a collodion membrane [Found: equiv., (*a*) 45·8, (*b*) 46·9. $(CO_2H)_2$ requires 45·0].

When the nearly colourless solution of the brown solid, obtained by treatment with norit, was titrated with permanganate, the end-points were indefinite, but this could not be traced to the effect of the norit. Since the brown, aqueous solution of the suboxide and the insoluble residue could be slowly and completely decolorised by acidified permanganate even in the cold, it would appear that the indefinite end-points might be due to the imperfect decoloration of the solution before titration. In view of the difficulty of obtaining a perfectly colourless solution and of the probable loss by adsorption on the norit, this method of decoloration was abandoned as unsuitable for further quantitative investigations. Nevertheless, a rough estimation was carried out and the results, although only approximate, are considered in the next section.

During attempts to scrape off the brown solid from the walls of the ozoniser, a curious phenomenon was observed on two occasions. The solid adhering to the outside of the inner tube was scraped with a nickel spatula into a glass basin. Almost immediately the solid in the basin glowed and gave off a white cloud with evolution of heat, and a dark, spongy mass resembling charcoal remained. When the contents of the basin were treated with water, the spongy mass floated and the water was not coloured, but was found to contain oxalic acid. It was thought that this curious phenomenon

might have been due to the accidental presence of moisture on the spatula or in the glass basin. When the brown solid was treated with water or methyl alcohol, a gas containing carbon dioxide was evolved, accompanied by a hissing noise which was more pronounced in the case of methyl alcohol. In order to ascertain if the gas was entirely carbon dioxide, a small glass bulb, h (Fig. 2A), was inserted between the reaction vessel, R, and the tap, T_8. Through a side tube of the bulb, water could be distilled into it from the vessel W, containing air-free water, and by placing a beaker of hot water underneath the bulb the water from the bulb could be distilled into the ozoniser. After some brown solid had been formed in the ozoniser and the latter evacuated, water was distilled into it as described. The gas evolved was carbon dioxide with a trace of carbon monoxide.

It follows from these preliminary experiments that the brown solid on treatment with water produces carbon dioxide, a brown solution containing oxalic acid and colloidal particles, and an insoluble, brown residue.

Quantitative Examination of the Brown Solid.—In order to determine whether the composition of the solid, produced under the conditions already described, varied with the pressure of the monoxide, as indicated by the earlier experiments (Part I), four samples prepared at 200, 350, 500, and 690 mm. were analysed by combustion in a stream of dry oxygen. The results showed that the substance contained carbon, hydrogen, and oxygen. Assuming that all the hydrogen in the material before combustion is present as water (possibly due to the absorption of atmospheric moisture during the transference from the reaction vessel and subsequent weighing), the atomic ratios of oxygen to carbon in the four samples of the brown solid were calculated to be, respectively, 0·58, 0·60, 0·60, and 0·59, each value being a mean of two determinations. There is thus a remarkable constancy in the ratio, corresponding to an empirical formula C_5O_3, throughout the range of pressure investigated; and it would appear that the compositions of the substances produced might be represented by the empirical formula C_5O_3,xH_2O. These conclusions suggest also that the product formed by streaming the gas through the discharge is not identical with that obtained from an enclosed mass of gas exposed to the discharge (compare Part I).

It has been mentioned that, under certain conditions, the brown solid reacts with water, evolving carbon dioxide. It was therefore necessary to determine whether any carbon dioxide was similarly evolved in the formation of the substance, C_5O_3,xH_2O, during the unavoidable hydration of the brown solid in manipulation. Analysis

of samples of the solid, prepared at 500 mm., collected from the inner tube of the reaction vessel in the presence of moist air, and from the outer tube under dry ether, showed that the latter contained the smaller amount of water, as calculated from the hydrogen content; the results corresponded with the empirical formulæ $C_5O_3,1{\cdot}95H_2O$ and $C_5O_3,1{\cdot}65H_2O$, respectively. They show that the ratio of carbon to oxygen is constant and independent of the water content of the substance, and they therefore afford evidence that carbon dioxide had not been liberated during the hydration of the brown solid. Experiments are in progress to determine whether the hydrogen content of the solid can be traced solely to the absorption of atmospheric moisture, or if it is due, in part, to the liberation of water from the walls of the reaction vessel during the discharge.

The increase in weight which took place when a known amount of the solid was exposed to moist air at atmospheric pressure is given in Table I.

TABLE I.

(Initial weight of solid = 0·02848 g.)

Time of exposure (hrs.)	0·5	1·75	2·5	3·5	27	70
Total increase in weight (mg.)	5·4	8·8	12·6	15·4	15·4	15·2

The substance was treated subsequently with excess of water, and the solution evaporated to dryness in a steam-oven; it had then suffered a total loss in weight of 0·00922 g., or 32·38%; 0·2427 g. of the same sample of brown solid, on direct treatment with water and subsequent evaporation to dryness, lost 0·0788 g., or 32·47% in weight. If it be assumed, in accordance with the experiments just described, that the increase in weight in moist air is due to the absorption of water only, then the observed increase corresponds to a change in composition from $C_5O_3,1{\cdot}70H_2O$ to $C_5O_3,4{\cdot}21H_2O$.

A further series of combustions was then carried out on samples obtained by treatment of the brown solid with water and subsequent evaporation to dryness in a steam-oven. The ratios of oxygen to carbon, computed as before, varied in an apparently chaotic manner with the pressure at which the brown solid had been formed. It would appear, however, that this erratic variation may be attributed to slow atmospheric oxidation of the suboxide residue after treatment with water and subsequent evaporation to dryness. Three successive combustions were carried out on the suboxide residue (original solid prepared at 200 mm.) so obtained, one in the forenoon, one in the afternoon, and the third on the next day. During this period the bulk of the substance, from which samples were taken for combustion, was exposed to the

atmosphere in a steam-oven (100°). The results (Table II) show that whilst the proportion of hydrogen is fairly constant, that of oxygen progressively increases, indicating that the brown solid after treatment with water absorbs oxygen while in contact with the atmosphere at 100°. No precautions were taken, in the experiments in which chaotic results were obtained, to insure that such atmospheric oxidation was avoided, or that the time of drying in the steam-oven was constant.

TABLE II.

Sequence of experiments.	I.	II.	III.
Carbon	1·00	1·00	1·00
Hydrogen	0·77	0·78	0·78
Oxygen	0·66	0·69	0·71

The results of these combustion experiments may now be summarised. In the pressure range investigated, the brown solid, after treatment with water and subsequent evaporation to dryness in a steam-oven, yields a substance which contains carbon, hydrogen, and oxygen, and slowly absorbs oxygen in air at 100°, but no definite composition can be assigned to it until samples have been prepared under conditions such that the possibility of oxidation is excluded during the treatment with water and subsequent drying.

Some further experiments, in which the volume of the monoxide consumed in the discharge was measured, were carried out on the evolution of gas which takes place when the brown solid is treated with water. After the discharge had been discontinued, the reaction vessel was evacuated; air-free water was then distilled into the vessel in the manner already described. After ½ hour had elapsed, the gases formed were pumped out and analysed, the results obtained being given in Table III. In the experiment (see below) in which 16·05 c.c. of gas were thus obtained, a further quantity of water was distilled into the reaction vessel, and the gases were pumped out after ½ hour. Less than 0·1 c.c. of gas, which proved to be carbon dioxide, was obtained. Repetitions of this procedure over a period of 5 days resulted in the formation of 3·0 c.c. of carbon dioxide.

TABLE III.

Pressure of CO (mm.).	200.	350.	500.
Volume of CO consumed (c.c. at *N.T.P.*)...	74·0	130·0	111·3
Volume of CO_2 formed (c.c. at *N.T.P.*).....	10·55	19·05	16·05
Volume of CO formed (c.c. at *N.T.P.*)	0·30	0·25	0·60

These results suggest that there is a rapid reaction associated with the formation of carbon dioxide together with small amounts of the monoxide, and a slow reaction also producing carbon dioxide.

It is important to note that the volume of dioxide produced by the rapid reaction is very nearly 1/7th of the volume of the monoxide used in the formation of the brown solid.

The behaviour of the nearly colourless aqueous solution of the brown solid towards permanganate solution has already been described. By rapid titration with standard permanganate solution, two approximate determinations have been carried out on the amount of oxalic acid formed when the solid is dissolved in water. Two samples of the solid, prepared at 500 mm., were found by combustion to have the empirical compositions (*a*) $C_5O_3,1{\cdot}70H_2O$, (*b*) $C_5O_3,1{\cdot}69H_2O$. About 0·5 g. of the solid was dissolved in water, and the solution diluted to 100 c.c.; 20 c.c. of this solution were decolorised by 0·25 g. of norit, a little dilute sulphuric acid was added, and the solution was heated to boiling and titrated rapidly. The results showed that 0·6490 g. of (*a*) and 0·5178 g. of (*b*) yielded 0·1180 and 0·0933 g., respectively, of oxalic acid calculated as anhydride, C_2O_3. Titration of a solution containing a similar amount of pure oxalic acid, which had been treated in the above manner with norit, showed that 1% of the oxalic acid had been adsorbed by the norit. The values obtained above for the equivalent weight of oxalic anhydride in the solution are therefore probably low by this amount.

On the basis of the provisional hypothesis that the empirical formula C_5O_3,xH_2O can be assigned to the brown solid, the amounts of oxalic anhydride ($M = 72$) which are equivalent to 1 g.-mol. of "C_5O_3" contained in the brown solid used in the above experiments are calculated to be (*a*) 25·22 g., and (*b*) 24·93 g., *i.e.*, approximately 3 mols. of empirical composition C_5O_3,xH_2O react with water to give 1 mol. of oxalic acid. Since the empirical composition of the solid is represented by C_5O_3,xH_2O, and since the hydrogen content must arise from the absorption of water by one or both of the processes already mentioned, it would appear that the formation of the brown solid may be represented by the equation $7CO = C_5O_3 + 2CO_2$. It will be recalled that in the reaction between water and the brown solid in the reaction vessel approximately 1 vol. of carbon dioxide was liberated for every 7 vols. of monoxide consumed in producing the solid. This observation suggests (the small amount of monoxide formed at the same time being neglected) that in the reaction with water each mol. of "C_5O_3" reacts forming 1 mol. of carbon dioxide.

By combining the results obtained from combustion, from titration of the nearly decolorised aqueous solution, and from the reaction with water, the following equation is advanced tentatively to represent the action of water on the brown solid after it has been removed

from the reaction vessel and exposed for a short time to atmospheric moisture:

$3C_5O_3,xH_2O + aq. = (CO_2H)_2 + 3CO_2 + 10C + (3x - 1)H_2O + aq.$

The production of free carbon, according to this equation, would account for the readiness with which the substance absorbs oxygen after treatment with water. Experiments are now in progress to determine the nature of the insoluble material formed when the brown solid is treated with water, and will form the subject of a future contribution.

Summary.

(1) A preliminary quantitative investigation has been carried out on the properties of the substance formed when carbon monoxide, at pressures from 200 to 690 mm. Hg, is subjected to ionisation by collision when streamed through an alternating electric field of the order of 20,000 volts per cm., and of frequency 250 cycles per sec.

(2) After removal from the reaction vessel, the substance has the empirical composition C_5O_3,xH_2O.

(3) The substance reacts with water, forming carbon dioxide, a brown solution containing oxalic acid and colloidal particles, and a dark, insoluble residue.

The authors wish to express their indebtedness to the Royal Commissioners of 1851 for a Senior Studentship which has enabled one of them (R. W. L.) to continue this research, and particularly to Professor F. G. Donnan, F.R.S., for his deep interest and advice during the development of this work.

The Sir William Ramsay Laboratories of Inorganic and Physical Chemistry,
University College, London. [*Received, February 10th*, 1927.]

CXXVII.—*The Vapour Pressure of Intensively Dried Nitrogen Tetroxide.*

By John William Smith.

The following experiments were commenced in 1925 with a view to extend the researches on the effect of intensive drying on physical properties. At that time, the only work on nitrogen tetroxide which had been carried out in this direction was due to H. B. Baker and Mrs. Baker (J., 1912, **101**, 2339), who had found that material which had been dried for more than a year boiled above 60°, whereas the normal b. p. is 22°, but no claim to great accuracy was made for this result on account of the small quantity of liquid available.

When the present work was nearly complete, however, a com-

munication on the same subject was published by Smits and his collaborators (J., 1926, 2657), who found that the vapour pressure of nitrogen tetroxide, unlike that of systems previously investigated, rises on intensive drying. The results of the present work, obtained quite independently, confirm those of Smits and extend them in certain directions.

EXPERIMENTAL.

Preparation of Materials.—The nitrogen tetroxide was prepared by the method of Cundall (J., 1891, **59**, 1077) in a modified form of the apparatus used by Ray (*J. Physical Chem.*, 1925, **29**, 74). It was redistilled four times in dry oxygen and stored in sealed tubes over phosphorus pentoxide.

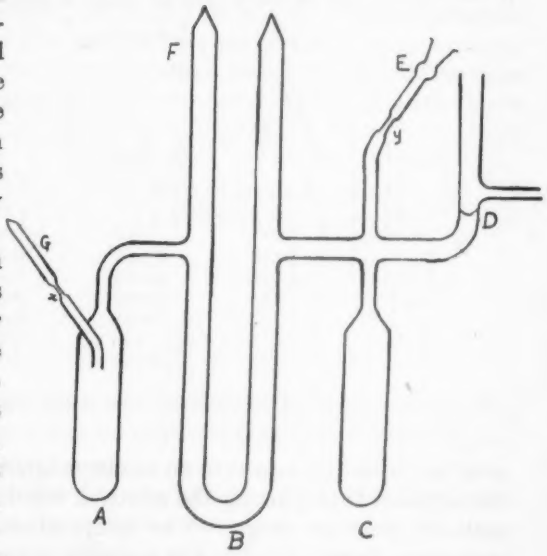
The phosphorus pentoxide was resublimed in pure dry oxygen in a horizontal tube of "Durosil" glass, with a side tube at the end remote from the oxygen inlet. This side tube was arranged to give a good sliding fit into the U-tube or other receiver for the sublimed material. Thus only a very narrow channel was left to allow the oxygen to escape, thereby preventing any access of moisture. The tube was well dried by passing dry oxygen through it whilst hot. It was charged by the tube-and-ramrod method described by Baker (*Phil. Trans.*, 1888, *A*, **179**, 573), with the oxygen current passing in the opposite direction. Sufficient material was introduced to eliminate the necessity of recharging during the sublimation process. The inlet tube was then inserted and the receiver slipped over the side tube. The phosphorus pentoxide was heated to 300° in a current of oxygen. Under these conditions, it sublimed steadily, condensing on the cooler part of the tube in light, feathery crystals, which were transferred to the receiver by turning a spiral rake.

Drying Apparatus.—For a more complete investigation of the properties of intensively dried nitrogen tetroxide, it was essential to secure a more rapid method of drying than that used heretofore. For this purpose, a slightly modified form of the apparatus used by Smits and Schoenmaker in their work on sulphur trioxide (J., 1924, **125**, 2554) was adopted. This was made of selected "Durosil" glass, as free as possible from streaks and air bubbles. The drying apparatus (Fig. 1) consisted of two bulbs, *A* and *C*, connected by a U-tube, *B*. The upper part of the tube from *C* ended in a tube, *E*, which could be connected to a high-vacuum pump system through a ground glass joint, whilst a side tube led to a sealed-in glass septum, *D*.

Procedure.—After thorough cleaning, all tubes except *E* were sealed off, and *E* was connected to the vacuum-pump system. Whilst under a high vacuum, the whole apparatus was maintained at 300° for 2 days. Dry air was now admitted, and tube *E* rapidly closed.

The end of tube *F* was cut off, and phosphorus pentoxide sublimed in, as already described. Careful tapping caused the pentoxide to pass round the bend into the further limb of the U-tube. In this way, *B* was filled almost completely in about 3 hours. With the oxygen current still passing, tube *F* was drawn off. Tube *G* was then reopened, and nitrogen tetroxide introduced from a storage bulb, bulb *A* being simultaneously cooled. Tube *G* was sealed off again at the constriction *x*. The tetroxide was then cooled in liquid air, *E* being connected again to the vacuum-pump system. Tube *E* was finally sealed off at the constriction *y* under a high vacuum. The tetroxide was then allowed to become warm. Distillations were carried out by immersing one bulb in ice and the other in water at room temperature, the baths being reversed every few hours.

Fig. 1.

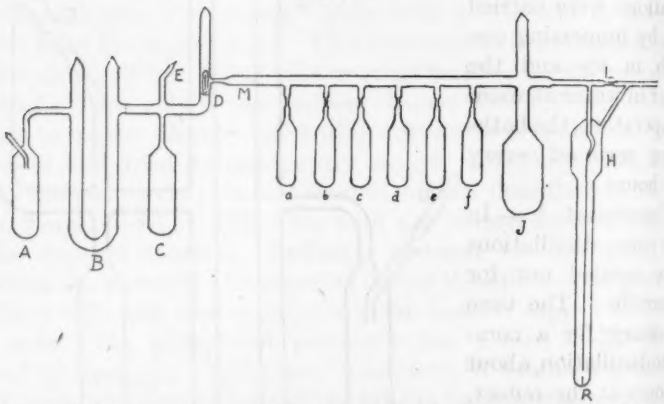


Experiment 1.—In this case distillations were carried out for 4 months. The time necessary for a complete distillation, about 3 hours at the outset, gradually increased as drying proceeded. Meanwhile a vapour-pressure apparatus was constructed of the form shown in Fig. 2. This consisted essentially of a long tube carrying a series of small bulbs provided with constrictions, and a bulb, *J*, to contain phosphorus pentoxide. One end of this long tube was connected to the inside of an all-glass pressure gauge of one of the forms described by Jackson (J., 1911, **99**, 1066). The outer jacket of this gauge was connected to a mercury manometer and to the vacuum-pump system. The two sides of the gauge were at first connected through a tube, *L*, with a constriction suitable for vacuum sealing. A breaker, consisting of a piece of stout capillary tubing with a short piece of soft iron inside, was now placed on the septum, *D*, of the drying apparatus. The tube *M* was then sealed to the T-piece above the septum, as shown in the diagram, and the vertical tube above the septum sealed off. The apparatus was now

evacuated to a pressure of 10^{-6} mm., the whole apparatus up to the septum being heated almost to softening point for 2 days. The top of the tube from J was then cut off, resublimed phosphorus pentoxide rapidly introduced, and the tube drawn off again. The evacuation and heating were then repeated for some days. The capillary, L, was sealed off while still under a high vacuum, and the apparatus allowed to stand for a few days. Meanwhile, the gauge was calibrated by admitting air to its outer sheath. The movement of the needle of the gauge with reference to a fixed pointer, R, was observed through a fixed cathetometer.

The nitrogen tetroxide was finally brought into bulb C, where it was frozen out in solid carbon dioxide and alcohol. The breaker

FIG. 2.



was then lifted by means of an electromagnet and dropped to break the septum, thus putting the nitrogen tetroxide vapour in contact with the pressure gauge. The temperature of the tetroxide was gradually allowed to rise, the pressure being roughly balanced by admitting air to the outer sheath of the gauge. The pressure was read off on the mercury gauge, fine corrections being calculated from the deflexion of the glass gauge from the normal. In this way, the vapour pressure was determined over the range 0—15°, giving the results shown in Table I.

TABLE I.

	Vapour pressures (mm.).				Vapour pressures (mm.).		
Temp.	Dry.	Wet.	Change.	Temp.	Dry.	Wet.	Change.
0·0°	266·3	264·0	+2·3	12·1°	493·7	489·5	+4·2
1·8	292·1	290·3	+1·8	14·6	559·5	554·2	+5·3
8·5	411·8	408·2	+3·6	15·0	571·2	565·0	+6·2

The values given under the heading "wet" were obtained by the author, using an apparatus of the type described above, with nitrogen

tetroxide that had been dried for a week over phosphorus pentoxide. The results agreed very well with the values obtained by Scheffer and Treub (*Z. physikal. Chem.*, 1912, **81**, 308).

The results with the dried material all tend to show a slight rise. There are, however, a few irregularities. These were explainable after the more thoroughly dried material had been examined in Expt. 2.

Bulb *f* was then slowly cooled in a freezing mixture and finally in solid carbon dioxide and alcohol. In this way, the nitrogen tetroxide in the gauge and tubes, presumably the more volatile portion, was condensed, and slow distillation occurred from the liquid in *C*. When about 5 c.c. had condensed, *C* was also cooled in carbon dioxide and alcohol, and bulb *f* sealed off. The temperature was again allowed to rise and the vapour pressure redetermined. This operation was repeated with bulbs *e* and *d*, the vapour pressure of the residue being taken on each occasion. The results are shown in Table II.

TABLE II.

No. of fraction removed.	Temp.	Vapour pressures (mm.). Dry.	Wet.	Change.
1	0·0°	265·3	264·0	+1·3
	14·7	560·4	557·3	+3·1
2	0·0	264·6	264·0	+0·6
	14·6	558·6	554·2	+4·4
3	0·0	263·1	264·0	−0·9
	14·7	561·0	557·3	+3·7

It would appear from these results that little, if any, separation of a more volatile from a less volatile component had been effected by this means.

Expt. 2.—The apparatus and method of drying employed were exactly the same as in the previous case, but the pressure-gauge portion was somewhat simplified, and made very much more compact, the fractionating bulbs being dispensed with. Thus this portion of the apparatus could be baked out much more readily than in the previous case. The whole apparatus, up to and including the glass spring gauge, was enclosed in a large air-thermostat during the pressure determination. The technique employed was similar to that in the previous case. In this apparatus there was only about one-half as much nitrogen tetroxide as in Expt. 1, whilst there was rather more phosphorus pentoxide. It had been drying for about 6 months, and during this time had been distilled to and fro nearly 400 times.

In order to obtain a full series of results before any possible reversion to the normal form could occur, the whole temperature range 0—30° was explored in one day. All the results tended to show a

distinct rise in the vapour pressure, but there were certain marked anomalies. It was found that although the apparatus was kept at constant temperature for more than an hour, the vapour pressure continued to rise, this rise being so slow that it was not at first noticed. Hence the time which had been allowed at each temperature for a constant vapour pressure to be established (about ½ hour) was clearly quite insufficient, although 10 minutes had sufficed with the undried material in a similar apparatus and under similar conditions. The value of the apparent "initial" vapour pressure, and also the rate of the change, seemed to depend on the previous history of the system. Thus, after the tetroxide had been frozen out in carbon dioxide and alcohol, the vapour pressure at 0° was some 6 hours in attaining a constant value, whilst the apparent "initial" vapour pressure was much greater when the liquid had only been cooled to about −10°. Hence the vapour pressures were determined at a few temperatures by allowing long periods for attainment of equilibrium; the results are in Table III.

TABLE III.

	Vapour pressures (mm.).				Vapour pressures (mm.).		
Temp.	Dry.	Wet.	Change.	Temp.	Dry.	Wet.	Change.
0·0°	282·6	264	+19	20·5°	757·9	736	+22
5·2	370·3	348	+22	24·2	890·5	869	+21
15·2	595·8	571	+25	24·7	910·3	890	+20
15·9	615·4	591	+24	29·0	1100·5	1080	+20
19·6	727·8	704	+24				

These values were all obtained about 10 days after the septum had been broken, when the vapour pressure at 0° appeared to remain steady. Some idea of the rate of reversion to the normal form was obtained by taking the vapour pressure at 0° on different days. This value fell from 286·8 mm. on the second day after breaking the septum to 282·6 mm. on the tenth day, *i.e.*, a drop in the abnormality from 23 to 19 mm. This slight reversion was apparently caused by the slow diffusion of moisture out of the less completely dried gauge portion of the apparatus.

That these rises in the vapour pressure were not due to any leakage in the apparatus during the 6 months' drying was shown by freezing out the nitrogen tetroxide in liquid air, whereupon no residual gas pressure was observed.

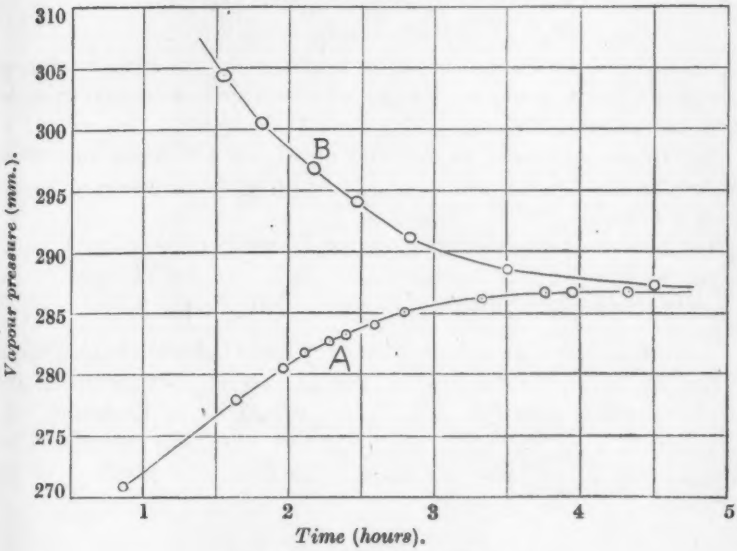
The slow establishment of a steady vapour pressure was further investigated. The liquid was cooled to about −10° for some 3 hours, and then immersed in pure ice and water, which was stirred continuously. Readings were taken at frequent intervals during 4 hours. The corresponding readings were also taken after the system had been cooled from 12° to 0°. The vapour pressure

time curves are shown in Fig. 3. These values were obtained on the second day after breaking the septum.

The high vapour pressures obtained and this slow change in the vapour pressure on standing at constant temperature seem to indicate that the equilibrium is shifted by the intensive drying, but at the stage when it was examined it was not completely fixed. Hence, when the temperature was raised, a corresponding, but slow, change occurred in the inner equilibrium, a less volatile component passing into a more volatile one. It would be natural to suppose that

FIG. 3.

Vapour pressure–time curves at 0°.



A. *After cooling to* −10°.
B. *After heating to* 19·6°.

intensive drying would affect the known inner equilibrium $N_2O_4 \rightleftharpoons 2NO_2$, but it is not possible to say, from the experiments recorded in this paper, to what extent changes in this equilibrium might account orthe observed phenomena.

Some indication of the form of a constant composition–vapour pressure curve was obtained by reaching equilibrium at one temperature, and then warming quickly to another temperature. These values can only be taken as approximate, however, as it is difficult to separate the two factors—ordinary thermal equilibrium and inner equilibrium. Two examples of the type of result obtained are given in Table IV. These values were obtained by reaching equilibrium at the temperature given in the first column, immersing

the liquid in a bath at the temperature shown in the second column, and taking the vapour pressure after 15 minutes.

TABLE IV.

Temp. at which equilibrium was attained.	Temp. of measurement.	Vapour pressure (mm.). After thermal equilibrium was established.	Normal.	Change.
0·0°	0·0°	282·6	264	+19
	9·4	437·2	428	+ 8
	12·6	505·2	503	+ 2
5·4	5·4	373·1	351	+22
	14·9	562·6	562	+ 0·6

Summary.

(*a*) It has been shown that after intensive drying at room temperature the vapour pressure of nitrogen tetroxide is increased throughout the range 0—30°.

(*b*) In accordance with the view developed by Smits, this would suggest a shift in the inner equilibrium towards the side of a more volatile component.

(*c*) The vapour pressure took a considerable time to reach a constant value. This is attributed to slow internal changes in the system, consequent upon temperature change.

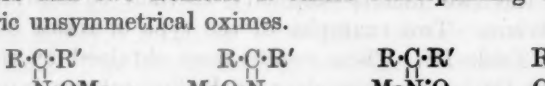
In conclusion, I desire to express my indebtedness to the Tuffnell Trustees for a Scholarship, to the Department of Scientific and Industrial Research for a grant, and especially to Professor F. G. Donnan, F.R.S., at whose suggestion this work was carried out, for his kindly advice and criticism throughout the progress of the research.

THE SIR WILLIAM RAMSAY INORGANIC AND PHYSICAL CHEMICAL LABORATORIES, UNIVERSITY COLLEGE, LONDON. [*Received, February 11th*, 1927.]

CXXVIII.—*The Isomerism of the Oximes. Part XXIX. Isomeric* p-*Nitrobenzyl and Methyl Ethers of Some Aldoximes.*

By OSCAR L. BRADY and LOUIS KLEIN.

THE Hantzsch–Werner theory demands the existence of two isomeric *O*-ethers and two isomeric *N*-ethers corresponding to a pair of isomeric unsymmetrical oximes.



The Beckmann structural theory as extended by Atack (J., 1921, **119**, 1175) demands one *O*-ether and two *N*-ethers,

$$CRR'{:}N{\cdot}OMe, \quad CRR'{<}\begin{matrix}NMe\\ O\end{matrix}, \quad CRR'{:}NMe{:}O.$$

Four isomeric methyl ethers have been obtained from certain unsymmetrical ketoximes (Semper and Lichtenstadt, *Ber.*, 1918, **51**, 928; Plowman and Whiteley, J., 1924, **125**, 587; Brady and Mehta, *ibid.*, p. 2297) but, despite many attempts, only one *N*-ether has been obtained from any one aldoxime (Brady, Dunn, and Goldstein, J., 1926, 2386). Now the gravamen of Atack's charge against the Hantzsch–Werner theory was the paucity of evidence for the existence of two isomeric *O*-ethers of undoubted composition. The best authenticated cases are the pairs of *O*-methyl ethers of *p*-nitrobenzophenoneoxime (Brady and Mehta, *loc. cit.*), *m*-nitrobenzaldoxime, and 3-nitro-4-methoxybenzaldoxime (Goldschmidt, *Ber.*, 1890, **23**, 2170; Brady and Dunn, J., 1913, **103**, 1620; Brady, Dunn, and Goldstein, J., 1926, 2402). In other cases, one or both of the isomerides are uncrystallisable oils (methyl ethers of *p*-tolylphenoximes, benzaldoximes, *p*-methoxy- and *o*-nitro-benzaldoximes), or the unstable is much more fusible than the stable isomeride and a mixture of the two melts at an intermediate temperature, so there is no satisfactory criterion of purity of the lower-melting compound (methyl, ethyl, and benzyl ethers of *p*-nitrobenzaldoximes). Even the evidence that the α- and β-*O*-methyl-*m*-nitrobenzaldoximes * are truly *O*-ethers is not entirely satisfactory.

The objects of the work here presented were (1) to adduce further evidence of the constitution of the two *O*-methyl-*m*-nitrobenzaldoximes, (2) the preparation of a number of pairs of *O*-ethers from various oximes, and (3) a further search for a second *N*-ether of aldoximes. The last effort was unavailing and no evidence was obtained of the existence of more than one *N*-ether corresponding to any one aldoxime. It has been found that both *O*-methyl-*m*-nitrobenzaldoximes have normal molecular weights and give quantitative yields of methyl iodide when heated with hydriodic acid. Further, a mixture of the two *O*-ethers has been obtained by the action of *O*-methylhydroxylamine on *m*-nitrobenzaldehyde, the α-isomeride greatly preponderating.

The evidence for the constitution of these compounds as *O*-ethers is therefore (1) methoxyl determinations, (2) synthesis from *O*-methylhydroxylamine, (3) partial conversion of the α- into the β-form by ultra-violet light (Brady and McHugh, J., 1924, **125**,

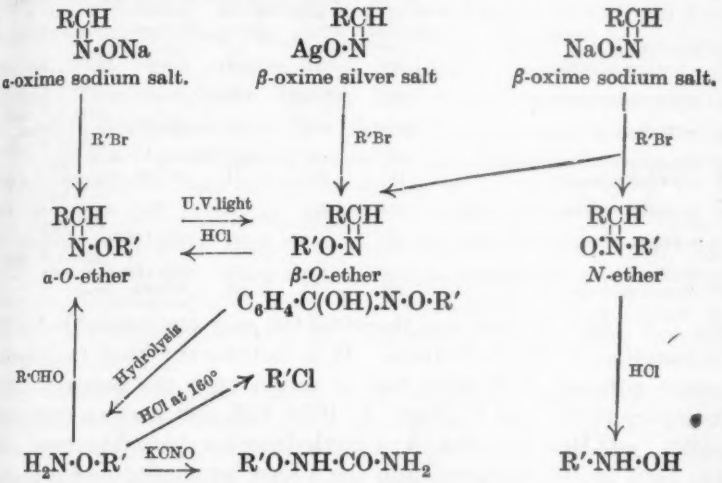
* The nomenclature used in this paper is that suggested by Brady and Bishop (J., 1925, **127**, 1361), and the new configurations have been adopted.

552), (4) complete conversion of the β- into the α-form by hydrogen chloride at room temperature (Goldschmidt and Kjellin, *Ber.*, 1891, **24**, 2555) and (5) normal molecular weights. None of this evidence rules out the structure RCH—N suggested as possible although

unlikely by Atack, who states that a substance having this structure should be readily convertible into the more stable form, >C:N·O·R. He has overlooked the rather surprising stability of the β-*O*-ethers in the absence of acids; *e.g.*, β-*O*-methyl-*m*-nitrobenzaldoxime is not isomerised on melting and can be kept unchanged for 16 years, whereas β-*m*-nitrobenzaldoxime is completely converted into the α-isomeride after 4 years. Moreover, the isomeric *O*-methyl-*p*-nitrobenzophenoneoximes are not interconvertible by means of hydrogen chloride (Brady and Mehta, *loc. cit.*). The ring formula is, however, inadmissible until some evidence is adduced for the existence of compounds of this type in which none of the four oxygen valencies is attached to a negative group—the compounds instanced by Atack (Kehrmann and Bohn, *Ber.*, 1914, **47**, 3052) are all salt-like in structure.

The chief difficulty experienced in previous work on the ethers of the aldoximes was the low melting point of the methyl, ethyl, and benzyl compounds and for this reason the *p*-nitrobenzyl derivatives have been studied, since compounds containing this radical have usually a higher melting point. As a result, three isomeric ethers, derived from each of ten pairs of isomeric oximes, have been prepared. One of the three was an *N*-ether as shown by its ready hydrolysis by acids to the aldehyde and *N*-*p*-nitrobenzylhydroxylamine and by its synthesis from these two compounds, the constitution of the latter of which was proved by Behrend and Leuchs and by Behrend and König (*Annalen*, 1890, **257**, 243; 1891, **263**, 190). The other two were *O*-ethers. This was established as follows. The previously unknown O-p-*nitrobenzylhydroxylamine* was prepared by the hydrolysis of *O*-*p*-nitrobenzylbenzhydroxamic acid (Werner, *Ber.*, 1892, **25**, 44), and its constitution proved by its conversion into *p*-nitrobenzyl chloride by heating under pressure with hydrochloric acid, by its reaction with potassium cyanate to give *p*-nitrobenzyloxycarbamide and by its failure to reduce cold Fehling's solution. This compound reacted with aldehydes, giving ethers identical with those obtained by the action of *p*-nitrobenzyl bromide on the sodium salts of the α-aldoximes, *i.e.*, the α-*O*-ethers. In six cases these α-*O*-ethers were converted by ultra-violet light into the β-*O*-ethers identical with those obtained by the action of *p*-nitrobenzyl bromide on the silver salts of the β-aldoximes. In all ten

cases the β-*O*-ethers were completely converted into the α-*O*-ethers by hydrogen chloride. These changes may be represented diagrammatically thus, R′ denoting $NO_2 \cdot C_6H_4 \cdot CH_2$:



The α-*O*-ethers are very stable towards hydrolysing agents, being unchanged by boiling with aqueous or alcoholic hydrochloric acid, hydrobromic acid, 60% sulphuric acid or 2*N*-sodium hydroxide.

The sodium salts of the α-oximes gave with *p*-nitrobenzyl bromide almost exclusively α-*O*-ethers; in only one case could any indication of the formation of the *N*-ether be detected (compare Brady, Dunn, and Goldstein, *loc. cit.*; Brady and Goldstein, J., 1926, 2403). The sodium salts of the β-oximes gave mainly the *N*-ethers, but small quantities of the β-*O*-ethers were also obtained in five cases. The β-*O*-ethers were generally prepared by the action of (1) *p*-nitrobenzyl bromide on either the β-aldoxime in the presence of dry silver oxide, or the silver salt of the β-aldoxime, (2) ultra-violet light on the α-*O*-ethers. The results are summarised in Table I.

As the melting points of the two isomeric *O*-ethers are frequently close together, the melting point of a mixture of approximately equal amounts of the two is given also; the figure for the two *O*-ethers of *p*-methoxybenzaldoxime is the m. p. of a mixture prepared by adding a very small quantity of the α- to the β-*O*-ether. That the β-*O*-ethers have been prepared by various methods is further evidence of their entity; a particular method was, however, not always equally successful and in some cases failed altogether.

The cases of Nos. 5 and 9 are of special interest, since all attempts to obtain the β-oximes have been unsuccessful (Brady and Dunn, J., 1923, **123**, 1787; Brady and Manjunath, J., 1924, **125**, 1066);

TABLE I.

p-Nitrobenzyl Ethers of Aldoximes.

	Oxime.	M. p. of *N*-ether.	M. p. of α-*O*-ether.	M. p. of β-*O*-ether.	Mixed m. p. of α-+β-*O*-ethers.	Methods of preparation of β-*O*-ethers.
1	Benzaldoxime	110°	60—61°	54°	37—38°	Ag salt.
2	*o*-Nitrobenzaldoxime	203	112	116	94—95	Ag_2O; Na salt; U.V. light.
3	*m*-Nitrobenzaldoxime	223	87—88	118	77—79	Ag_2O; Ag salt; Na salt; U.V. light.
4	*p*-Nitrobenzaldoxime	234—235	179	184	153—155	Ag_2O; Ag salt; Na salt; U.V. light.
5	*o*-Methoxybenzaldoxime	141	88	Oil.	—	U.V. light.
6	*p*-Methoxybenzaldoxime	150	122	74	69—70	Ag salt; Na salt; U.V. light.
7	3 : 4-Methylenedioxybenzaldoxime	144	110	125	95	Ag_2O; Ag salt; U.V. light.
8	3-Nitro-4-methoxybenzaldoxime	232	117	152	108—109	Ag_2O; Ag salt; Na salt; U.V. light.
9	5-Nitro-2-methoxybenzaldoxime	237	149	153	128—130	U.V. light.
10	Cinnamaldoxime	135	83	86	62—63	Ag_2O.

the U.V. light method was therefore the only one available for the preparation of the β-*O*-ethers. It is noteworthy that conversion occurs although U.V. light has no action upon the parent oximes (compare Brady and McHugh, J., 1924, **125**, 552, and experimental part). α-*O*-Methyl-6-nitro-3 : 4-methylenedioxybenzaldoxime also has been partly converted into the β-form by similar means; only one form of the oxime is known.

The *N*-ethers of *o*-methoxy- and 5-nitro-2-methoxy-benzaldoximes were obtained from the aldehydes and *N*-*p*-nitrobenzylhydroxylamine, since the β-oximes are unknown.

The action of *p*-nitrobenzyl bromide on the sodium salt of β-cinnamaldoxime produced a viscous, brown oil which could not be purified. The *N*-ether was, however, easily prepared by the action of *N*-*p*-nitrobenzylhydroxylamine on the aldehyde. It behaved abnormally on hydrolysis, giving a product which could not be satisfactorily purified. This peculiar behaviour is being further investigated (compare Bamberger and Weitnauer, *Ber.*, 1922, **55**, 3376).

The *N*-*p*-nitrobenzyl ethers undergo the Beckmann change in the same way as the *N*-methyl ethers (Brady and Dunn, J., 1926, 2411).

Finally the binary fusion diagram for α-benzaldoxime and *p*-nitrobenzyl bromide was constructed, but no evidence of compound formation was forthcoming (compare Brady and Truszkowski, J., 1924, **125**, 1089; Brady and Klein, J., 1925, **127**, 852).

We consider that the results here described remove all doubt of the existence of two isomeric *O*-ethers. Any theory of the isomerism of the oximes must therefore provide for two such compounds and, so far, only that suggested by Hantzsch and Werner makes a serious attempt to do so.

EXPERIMENTAL.

Action of p-*Nitrobenzyl Bromide on Sodium Salts of α-Aldoximes.*

α-Benzaldoxime.—The oxime (8 g.) dissolved in alcohol (20 c.c.) was mixed with sodium ethoxide (from 1·53 g. of sodium in 40 c.c. of alcohol), and a hot solution of *p*-nitrobenzyl bromide (14·4 g.) in alcohol (100 c.c.) added. Having been heated on the water-bath for ½ hour, the mixture was diluted with water (250 c.c.) and cooled in ice. The α-*O*-*p*-nitrobenzylbenzaldoxime thus obtained, in 89% yield, crystallised from alcohol in almost white prisms, m. p. 60—61° (Found: N, 11·1; *M*, cryoscopic in benzene, 253. Calc.: N, 10·9%; *M*, 256). Schroeter and Peschkes (*Ber.*, 1900, **33**, 1982) described the compound as forming yellow prisms. The ether was unaffected by boiling with hydrochloric acid (aqueous or alcoholic), hydrobromic acid, 60% sulphuric acid or with sodium hydroxide solution.

The aqueous-alcoholic filtrate from the above preparation was extracted with chloroform, and the extract was washed with 2*N*-sodium hydroxide, to remove unchanged oxime, and with water, evaporated to small bulk, and dried over sodium sulphate. Treatment with dry hydrogen chloride for an hour produced a small precipitate (m. p. 172—173°) of *N*-*p*-nitrobenzylhydroxylamine hydrochloride, decomposition of which with aqueous sodium carbonate gave a small quantity of *N*-*p*-nitrobenzylhydroxylamine (m. p. 120°), identified by comparison with an authentic specimen.

α-Cinnamaldoxime.—By the above method (oxime, 2·72 g. in 15 c.c. of alcohol; sodium ethoxide from 0·43 g. of sodium and 20 c.c. of alcohol; *p*-nitrobenzyl bromide, 4 g. in 40 c.c. of alcohol) a 69% yield was obtained of α-O-p-*nitrobenzylcinnamaldoxime*, which crystallised from alcohol in buff leaflets, m. p. 83° (Found: N, 10·2; *M*, cryoscopic in benzene, 271. $C_{16}H_{14}O_3N_2$ requires N, 9·9%; *M*, 282).

α-o-*Nitrobenzaldoxime.*—Owing to the sensitiveness of this oxime to hot alkali, the reaction was carried out at room temperature. The oxime (5 g.) in 30 c.c. of cold alcohol was treated with sodium ethoxide (from 0·7 g. of sodium and 30 c.c. of alcohol), a warm solution of *p*-nitrobenzyl bromide (6·5 g. in 80 c.c. of alcohol) added, and the mixture immediately cooled; a yellow solid then separated. After 12 hours, the precipitate was collected (84% yield), and crystallised from alcohol, α-O-p-*nitrobenzyl*-o-*nitrobenzaldoxime* being obtained in pale yellow leaflets, m. p. 112° (Found: N, 13·9; *M*, cryoscopic in camphor, 295. $C_{14}H_{11}O_5N_3$ requires N, 14·0%; *M*, 301).

The alcoholic filtrate from the preparation was diluted and

treated as described under benzaldoxime, but nothing crystalline was isolated.

α-m-*Nitrobenzaldoxime*.—The oxime (8 g., suspended in 25 c.c. of alcohol), sodium ethoxide (from 1·11 g. of sodium and 40 c.c. of alcohol), and *p*-nitrobenzyl bromide (10·4 g. in 75 c.c. of hot alcohol) were heated on the water-bath under reflux for 30 minutes. On cooling, an oil separated which soon solidified (yield 90%). This crystallised from alcohol containing a little acetone, α-O-p-*nitrobenzyl*-m-*nitrobenzaldoxime* being obtained in pale yellow prisms, m. p. 87—88° (Found : N, 14·1 ; *M*, cryoscopic in benzene, 284. $C_{14}H_{11}O_5N_3$ requires N, 14·0% ; *M*, 301). The compound is dimorphous, for when its concentrated alcoholic solution is slowly cooled without stirring, pale yellow prisms, m. p. 97°, are obtained and a solution of these in hot alcohol, on being cooled rapidly and stirred, deposits the lower-melting form. A mixture of approximately equal amounts of either form with β-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime melts at 77—79°.

α-p-*Nitrobenzaldoxime*.—The O-p-*nitrobenzyl ether*, prepared similarly to the *m*-compound in 88% yield, crystallises from acetone in glistening, pale yellow prisms, m. p. 179° (Found : N, 13·9. $C_{14}H_{11}O_5N_3$ requires N, 14·0%).

α-3 : 4-*Methylenedioxybenzaldoxime*.—The addition of *p*-nitrobenzyl bromide (10·5 g. in 100 c.c. of hot alcohol) to a solution of the oxime (8 g. in 60 c.c. of warm alcohol) mixed with sodium ethoxide (from 1·12 g. of sodium and 40 c.c. of alcohol) gave a precipitate which dissolved when the mixture was heated under reflux for 30 minutes. On cooling, a mass of yellow crystals separated and, after dilution with a little water, these were collected (yield 96%) and crystallised from acetone; α-O-p-*nitrobenzyl*-3 : 4-*methylenedioxybenzaldoxime* was then obtained in pale yellow prisms, m. p. 110° (Found : N, 9·4; *M*, cryoscopic in camphor, 315. $C_{15}H_{12}O_5N_2$ requires N, 9·3% ; *M*, 300).

α-p- *and* α-o-*Methoxybenzaldoximes*.—Treated as described above with sodium ethoxide (from 0·92 g. of sodium and 40 c.c. of alcohol) and *p*-nitrobenzyl bromide (8·58 g. in 80 c.c. of alcohol), these oximes (6 g. in 50 c.c. of alcohol) gave, respectively, an 84% yield of α-O-p-*nitrobenzyl*-p-*methoxybenzaldoxime*, pale yellow prisms from acetone, m. p. 122° (Found : N, 9·7. $C_{15}H_{14}O_4N_2$ requires N, 9·8%), and a 79% yield of α-O-p-*nitrobenzyl*-o-*methoxybenzaldoxime*, very pale yellow prisms from methyl alcohol, m. p. 88° (Found : N, 9·9%).

α-3-*Nitro*-4-*methoxy*- *and* α-5-*Nitro*-2-*methoxy*-*benzaldoximes*.—Treated as described above with sodium ethoxide (from 0·59 g. of sodium and 30 c.c. of alcohol) and *p*-nitrobenzyl bromide (5·51 g.

in 35 c.c. of hot alcohol), the oximes (5 g. in 40 c.c. of alcohol) gave, respectively, a 90% yield of α-O-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime*, a pale yellow, micro-crystalline powder from amyl alcohol, m. p. 117° (Found: N, 12·8; *M*, cryoscopic in camphor, 340. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331), and an 87% yield of α-O-p-*nitrobenzyl*-5-*nitro*-2-*methoxybenzaldoxime*, white, micro-crystalline needles from acetone, m. p. 149° (Found: N, 12·7%; *M*, cryoscopic in camphor, 328).

α-*O*-*p*-Nitrobenzyl-3-nitro-4-methoxybenzaldoxime is dimorphous like the derivative from *m*-nitrobenzaldoxime, separating from benzene in yellow prisms, m. p. 105°.

O-p-*Nitrobenzylhydroxylamine.*

Benzhydroxamic Acid.—Jeanrenaud (*Ber.*, 1889, **22**, 1272) obtained this compound in 40% yield, but more than 60% can be obtained by the following modification of his process. Hydroxylamine hydrochloride (23·2 g.) was dissolved in the minimum amount of water, and alcohol (50 c.c.) added followed by alcoholic sodium ethoxide (7·7 g. of sodium in 180 c.c. of alcohol). The precipitated sodium chloride was filtered off, and ethyl benzoate (50 g.) added followed by more sodium ethoxide (7·7 g. of sodium in 180 c.c. of alcohol). On cooling, the liquid set to a mass of crystals of sodium benzhydroxamate, which were collected, washed with alcohol, dried, and dissolved in the minimum of water. The solution was acidified with hydrochloric acid and extracted six times with chloroform; the extract on evaporation yielded benzhydroxamic acid sufficiently pure for the next preparation.

O-p-*Nitrobenzylbenzhydroxamic Acid*, $C_6H_5{\cdot}C(OH){:}N{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$ or $C_6H_5{\cdot}CO{\cdot}NH{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$.—A solution of benzhydroxamic acid (25 g.) in alcohol (80 c.c.) was mixed with a solution of potassium hydroxide (10·2 g.) in water (40 c.c.), *p*-nitrobenzyl bromide (39·4 g. in 300 c.c. of hot alcohol) added, and the mixture heated under reflux for 45 minutes. On cooling, *O*-*p*-nitrobenzylbenzhydroxamic acid separated and was crystallised from alcohol (compare Werner, *Ber.*, 1892, **25**, 44).

O-p-*Nitrobenzylhydroxylamine.*—*O*-*p*-Nitrobenzylbenzhydroxamic acid (15 g.) in hot alcohol (125 c.c.) was boiled under reflux for 25 minutes with concentrated hydrochloric acid (150 c.c.). The clear solution thus obtained was cooled somewhat and diluted with water (150 c.c.) and while still warm was extracted with chloroform (200 c.c.) to remove benzoic acid, etc. The extraction was carried out as rapidly as possible, since, when the liquid cooled, the sparingly soluble *O*-*p*-nitrobenzylhydroxylamine hydrochloride was apt to separate. The aqueous layer was evaporated to dryness on the

water-bath; a 96% yield of the crude compound was then obtained. The residue was crystallised from hot 2*N*-hydrochloric acid and the crystals were washed with alcohol and then with ether, pure O-p-*nitrobenzylhydroxylamine hydrochloride* being obtained in white leaflets, m. p. 217° (decomp.) (Found: Cl, 17·9. $C_7H_8O_3N_2$,HCl requires Cl, 17·3%). Boiling with water produces partial hydrolysis, and, unlike *N*-*p*-nitrobenzylhydroxylamine, the compound does not reduce Fehling's solution. The hydrochloride was dissolved in a little hot water, containing hydrochloric acid, and a solution of potassium cyanate added; p-*nitrobenzyloxycarbamide* separated on cooling and crystallised from hot water in white prisms, m. p. 206° (decomp.) (Found: N, 20·1. $C_8H_9O_4N_3$ requires N, 19·9%).

O-*p*-Nitrobenzylhydroxylamine hydrochloride (0·5 g.) was heated in a sealed tube at 160—180° for 4 hours with concentrated hydrochloric acid (2 c.c.). After cooling, the liquid contained a few colourless plates of the unchanged compound and some brown lumps; the latter were crystallised from light petroleum, and the *p*-nitrobenzyl chloride thus obtained was identified by comparison with an authentic specimen and by conversion into *p*-nitrobenzyl iodide by boiling in alcohol with potassium iodide. The hydrochloric acid mother-liquor on evaporation yielded ammonium chloride. When a concentrated solution of the hydrochloride in hot water, containing hydrochloric acid, was poured with stirring into an excess of 2*N*-sodium carbonate, an emulsion was obtained which, on cooling in ice, deposited crystals of the free base; a further quantity was obtained by extracting the mother-liquor with chloroform. After crystallising from light petroleum containing a little benzene, O-p-*nitrobenzylhydroxylamine* was obtained in white prisms, m. p. 56° (Found: N, 16·9. $C_7H_8O_3N_2$ requires N, 16·7%).

Action of O-p-*Nitrobenzylhydroxylamine on Aldehydes.*

p-Nitrobenzaldehyde (1·5 g.) in hot alcohol was treated with a solution of *O*-*p*-nitrobenzylhydroxylamine hydrochloride (2 g.) in hot 2*N*-hydrochloric acid (20 c.c.); crystals of α-*O*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime soon began to separate. After cooling, they were collected and washed with alcohol (yield 2 g.).

By similar methods, like results were obtained with *o*-nitrobenzaldehyde, 5-nitro-2-methoxybenzaldehyde, and 3 : 4-methylenedioxybenzaldehyde, except that in the last case the mixture was heated for a short time on the water-bath.

m-Nitrobenzaldehyde (0·9 g.) in warm alcohol (15 c.c.) was mixed with a solution of *O*-*p*-nitrobenzylhydroxylamine (1·05 g.) in warm alcohol (12 c.c.); after 3 days, crystals of α-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime had separated (yield 1·6 g.). The alcoholic

mother-liquor was fractionally precipitated with water, but only a small amount of the α-*O*-ether was obtained and there was no indication of the presence of the β-*O*-ether. The α-*O*-ethers were similarly obtained from cinnamaldehyde and *p*-methoxybenzaldehyde and *O*-*p*-nitrobenzylhydroxylamine. In every case the *O*-ether was identified by the method of mixed melting points with that obtained by the action of *p*-nitrobenzyl bromide on the sodium salt of the α-oxime.

Action of Silver Oxide and p-*Nitrobenzyl Bromide on* β-*Aldoximes.*

β-*Cinnamaldoxime.*—The oxime (2·94 g.) and *p*-nitrobenzyl bromide (4·32 g.) were dissolved in hot benzene (30 c.c.), dry, finely powdered silver oxide (2·6 g.) was added, and the mixture was boiled under reflux for an hour. After silver oxide and bromide had been removed, the solution was allowed to evaporate spontaneously. The residual solid was pressed on a porous tile, washed with 2*N*-sodium hydroxide to remove unchanged oxime and with water, and crystallised twice from methyl alcohol; β-O-p-*nitrobenzylcinnamaldoxime* was then obtained in pale buff prisms, m. p. 86° (yield 1·5 g.) (Found: N, 10·0; *M*, cryoscopic in benzene, 280. $C_{16}H_{14}O_3N_2$ requires N, 9·9%; *M*, 282).

β-o- *and* β-m-*Nitrobenzaldoximes.*—The finely powdered oxime (1 g.) and *p*-nitrobenzyl bromide (1·3 g.) were dissolved in benzene (75 c.c.) at room temperature, dry silver oxide (1 g.) was added, and the mixture was kept for 5 days in the dark in a corked flask with occasional shaking. The mixture was then heated to boiling and filtered hot. The filtrate on spontaneous evaporation gave a sticky solid which, after being pressed on a porous tile and crystallised four times from alcohol, yielded β-O-p-*nitrobenzyl*-o-*nitrobenzaldoxime* in feathery needles, m. p. 116° (Found: N, 13·7; *M*, cryoscopic in camphor, 312. $C_{14}H_{11}O_5N_3$ requires N, 14·0%; *M*, 301). Similarly, β-O-p-*nitrobenzyl*-m-*nitrobenzaldoxime* was obtained, crystallising from methyl alcohol in white leaflets, m. p. 118° (Found: N, 14·0%; *M*, cryoscopic in ethylene dibromide, 326).

β-p-*Nitro- and* β-3 : 4-*Methylenedioxy-benzaldoximes.*—The finely powdered oxime (3 g.) and *p*-nitrobenzyl bromide (3·9 g.) were suspended in benzene (250 c.c.) at room temperature, dry silver oxide (3 g.) was added, and the mixture was kept in the dark in a corked flask for 6 days with occasional shaking. After being heated to boiling and filtered, the solution gave on evaporation a solid which was washed with 2*N*-sodium hydroxide, water, and a little warm acetone. The residue on crystallisation from acetone gave β-O-p-*nitrobenzyl*-p-*nitrobenzaldoxime* as a white, micro-crystalline powder,

m. p. 184° (Found : N, 13·8. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). Similarly, β-O-p-*nitrobenzyl*-3 : 4-*methylenedioxybenzaldoxime* was obtained in yellow prisms, m. p. 125° (Found : N, 9·5; *M*, cryoscopic in camphor, 325. $C_{15}H_{12}O_5N_2$ requires N, 9·3%; *M*, 300).

β-3-*Nitro*-4-*methoxybenzaldoxime*.—By a similar method to the preceding, from the oxime (2·7 g.), *p*-nitrobenzyl bromide (2·97 g.), benzene (500 c.c.), and silver oxide (1·9 g.), β-O-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime* was obtained; it crystallised from alcohol-acetone in white needles, m. p. 152° (Found : N, 12·8; *M*, cryoscopic in camphor, 348. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331).

β-*Benzaldoxime and* β-p-*Methoxybenzaldoxime*.—β-Benzaldoxime gave only an uncrystallisable oil by the silver oxide method. β-*p*-Methoxybenzaldoxime gave only the α-*O*-*p*-nitrobenzyl ether, although various solvents and other modifications of procedure were tried. The β-*O*-ethers from these two oximes have, however, been prepared by another method (see below).

Action of p-*Nitrobenzyl Bromide on Silver Salts of* β-*Aldoximes.*

β-*Benzaldoxime*, β-p-*Methoxy-*, β-p-*Nitro-*, *and* β-3-*Nitro*-4-*methoxy-benzaldoximes*.—The silver salts were each prepared by suspending the oxime in alcohol, adding an alcoholic solution of sodium ethoxide prepared from a weighed quantity of sodium, shaking the mixture until a clear solution was obtained, and then adding in artificial light an aqueous-alcoholic solution of silver nitrate. The precipitated silver salt, which was usually difficult to filter off, was collected and washed first with absolute alcohol and then with dry chloroform. The quantities used for β-benzaldoxime, β-*p*-methoxybenzaldoxime, β-*p*-nitrobenzaldoxime and β-3-nitro-4-methoxybenzaldoxime, respectively, were oxime (7·2 g.; 5·5 g.; 1·45 g.; 4·35 g.), alcohol (50 c.c.; 50 c.c.; 20 c.c.; 60 c.c.), sodium (1·37 g. in 70 c.c. of alcohol; 0·83 g. in 50 c.c.; 0·2 g. in 15 c.c.; 0·51 g. in 30 c.c.), silver nitrate (11 g. in the minimum of water, and 80 c.c. of alcohol added; 6·5 g., and 75 c.c. of alcohol; 2 g., and 15 c.c. of alcohol; 4 g., and 30 c.c. of alcohol). The silver salt so obtained was suspended in a solution of *p*-nitrobenzyl bromide in chloroform and kept in a corked flask in the dark for a week with occasional shaking. The quantities were *p*-nitrobenzyl bromide (9 g.; 4 g.; 1·3 g.; 3·2 g.), chloroform (100 c.c.; 45 c.c.; 30 c.c.; 55 c.c.) respectively. The solution was then filtered, and the chloroform allowed to evaporate spontaneously. In the case of β-benzaldoxime, great difficulty was experienced at first in inducing the residual oil to crystallise. This was overcome by seeding the oil with a little of the crude product of the action of *p*-nitrobenzyl bromide on the sodium salt of β-benzaldoxime and keeping it in an

evacuated desiccator for a week in an ice-chest; the pasty mass thus obtained was pressed on a porous tile. Later, when the pure β-*O*-ether was available, it was sufficient to seed the oil with this, keep it as before for 2 days, and press the solid on a tile. In this way, 3·6 g. of a nearly pure product were obtained. On crystallising from alcohol with seeding, β-O-p-*nitrobenzylbenzaldoxime* was obtained in pale yellow crystals, m. p. 54° (Found: N, 11·1; *M*, cryoscopic in benzene, 247. $C_{14}H_{12}O_3N_2$ requires N, 10·9%; *M*, 256). Similarly, after crystallising from acetone and water and then from methyl alcohol, β-O-p-*nitrobenzyl*-p-*methoxybenzaldoxime* was obtained in fine, white needles, m. p. 74° (Found: N, 9·9. $C_{15}H_{14}O_4N_2$ requires N, 9·8%).

The addition of a small amount of α-*O*-*p*-nitrobenzyl-*p*-methoxybenzaldoxime (m. p. 122°) lowered the melting point of the above compound to 69°; with somewhat larger quantities of the α-ether, the mixed melting point lay between 74° and 122°. The β-*O*-*p*-nitrobenzyl ethers of *m*-nitro-, *p*-nitro-, 3 : 4-methylenedioxy-, and 3-nitro-4-methoxy-benzaldoximes were prepared analogously from the silver salts of the respective β-oximes and found to be identical with the compounds obtained from these oximes by the silver oxide method.

Action of Ultra-violet Light on α-O-p-*Nitrobenzyl Ethers.*

The method consisted in exposing a solution of the α-*O*-*p*-nitrobenzyl ether in benzene in a silica vessel to the light of a quartz mercury-vapour lamp at a distance of about 5 inches. The exposure was usually continuous for 72 hours. The benzene was then removed and the crude product, after its melting point had been determined, was fractionally crystallised from suitable solvents. Unless the contrary is mentioned, the products were identified by the method of mixed melting points with ethers otherwise prepared, mixed melting points being taken with both α- and β-ethers.

α-O-p-*Nitrobenzyl*-o-*nitrobenzaldoxime* (m. p. 112°; 1 g. in 25 c.c. of benzene).—The crude product (m. p. 91—92°) was dissolved in the minimum of boiling alcohol; on cooling, crystals, m. p. 99—101°, separated which, on recrystallisation from alcohol, gave unchanged α-*O*-ether. The mother-liquor from the first crystallisation, on being diluted somewhat with water and scratched, gave crystals (m. p. 97—106°) which, recrystallised three times from alcohol, gave the pure β-*O*-ether (m. p. 116°).

α-O-p-*Nitrobenzyl*-m-*nitrobenzaldoxime* (m. p. 87—88°; 1·5 g. in 25 c.c. of benzene).—The crude product (m. p. 73—77°) was dissolved in a small quantity of hot alcohol, containing a little acetone, and the solution cooled with stirring; the product, m. p. 76—78°,

thus obtained crystallised from a fairly large volume of alcohol, containing a little acetone, a compound, m. p. 103—104°, being obtained which, after two crystallisations from methyl alcohol, yielded the pure β-*O*-ether (m. p. 118°).

α-O-p-*Nitrobenzyl*-p-*nitrobenzaldoxime* (m. p. 179°; 2 g. in 150 c.c. of benzene).—The crude product (m. p. 150—151°) was treated with boiling acetone, partial solution occurring. The solution was decanted while hot, and the residue, after two crystallisations from much acetone, gave the pure β-*O*-ether (m. p. 184°). The acetone extract, on cooling, gave crystals (m. p. 156—158°) which, after repeated crystallisation from acetone, gave more β-*O*-ether. The mother-liquor from the crystals (m. p. 156—158°) was diluted with water and the precipitate produced was crystallised from acetone; the pure α-*O*-ether was then obtained.

α-O-p-*Nitrobenzyl*-3 : 4-*methylenedioxybenzaldoxime* (m. p. 110°; 1 g. in 40 c.c. of benzene; exposure, 68 hours).—The residue (m. p. 75—90°), after being pressed on a porous tile and washed with a little ether, was dissolved in a hot mixture of alcohol and acetone, and the solution, after cooling, was fractionally precipitated with water. The first and the second fraction, after crystallisation from acetone and water and then from acetone, gave unchanged α-*O*-ether. The third fraction, m. p. 80—85°, crystallised from acetone and water and then from alcohol, gave a very small quantity of somewhat impure β-*O*-ether (m. p. 120°).

α-O-p-*Nitrobenzyl*-p-*methoxybenzaldoxime* (m. p. 122°; 1·5 g. in 45 c.c. of benzene; exposure, 100 hours).—The residue (m. p. 100—105°), on crystallisation from acetone, gave unchanged α-*O*-ether; addition of a little water to the acetone filtrate gave another crop of this compound. The aqueous-acetone filtrate, on spontaneous evaporation, yielded a pasty solid which was pressed on a porous tile and crystallised twice from methyl alcohol; a very small yield of β-*O*-ether was then obtained.

α-O-p-*Nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime* (m. p. 117°; 0·75 g. in 45 c.c. of benzene).—The crude product (m. p. 115—126°) was crystallised from benzene and then twice from acetone–alcohol, the pure β-*O*-ether being obtained. The benzene mother-liquor gave only impure β-*O*-ether.

α-O-p-*Nitrobenzyl*-o-*methoxybenzaldoxime* (m. p. 88°; 1·5 g. in 25 c.c. of benzene; exposure, 100 hours).—The crude product (m. p. 78—80°), on crystallisation from alcohol, gave the α-*O*-ether; a second crop of the same compound was obtained by diluting the filtrate with a little water. The aqueous-alcoholic filtrate, on spontaneous evaporation, gave an oil which would not crystallise on being seeded with the α-*O*-ether. It undoubtedly contained the

unknown β-*O*-ether, for, after hydrogen chloride had been passed into its chloroform solution and the solvent evaporated, the residue immediately solidified on being scratched and was then found to be almost pure α-*O*-ether (compare below).

α-O-p-*Nitrobenzyl-5-nitro-2-methoxybenzaldoxime* (m. p. 149°; 3 g. in 150 c.c. of benzene; exposure, 96 hours).—The crude product (m. p. 123—126°) was dissolved in 40 c.c. of boiling acetone and, after cooling, fractionally precipitated with water. The first fraction (m. p. 132—139°), after three crystallisations from acetone–alcohol, gave 0·5 g. of β-O-p-*nitrobenzyl-5-nitro-2-methoxybenzaldoxime* in white needles, m. p. 153° (Found: N, 12·8; *M*, cryoscopic in camphor, 357. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331). Admixture with the α-*O*-ether caused a depression of melting point to 128—130°.*

Action of Hydrogen Chloride on β-O-p-*Nitrobenzyl Ethers.*

Hydrogen chloride was passed for 10—20 seconds into a solution of a small quantity of the β-*O*-ether in a little chloroform. The solution was then evaporated, and the product (after crystallisation from alcohol in the case of the ether of cinnamaldoxime) identified as the corresponding α-*O*-ether by the method of mixed melting points. From the ether of benzaldoxime an oil was obtained which, however, immediately solidified on being seeded with a crystal of the α-*O*-ether. With the ethers of *m*-nitro- and 3-nitro-4-methoxybenzaldoximes the oils obtained solidified on being rubbed with a little alcohol. The results are in Table II.

TABLE II.

	Before HCl treatment.		After HCl treatment.		
O-p-Nitrobenzyl ether of	M. p.	Mixed m. p. with α-*O*-ether.	M. p.	Mixed m. p. with α-*O*-ether.	M. p. of α-*O*-ether.
β-Cinnamaldoxime	86°	62—63°	77—79°	81—82°	83°
β-Benzaldoxime	54	37—38	57—58	59	60—61
β-*o*-Nitrobenzaldoxime	116	94—95	107—108	110—111	112
β-*m*-Nitrobenzaldoxime	118	77—79	82—83	85—86	87—88
β-*p*-Nitrobenzaldoxime	184	153—155	174—175	177—178	179
β-3 : 4-Methylenedioxybenzaldoxime	125	95	105	107	110
β-*p*-Methoxybenzaldoxime	74	69—70	115—117	119—120	122
β-3-Nitro-4-methoxybenzaldoxime	152	108—109	105—106	111—112	117
β-*o*-Methoxybenzaldoxime	Oil.	—	74—76	78—80	88
β-5-Nitro-2-methoxybenzaldoxime	153	128—130	146	148	149

* Exposure of a benzene solution of α-5-nitro-2-methoxybenzaldoxime to ultra-violet light for 48 hours did not result in its conversion into the β-isomeride.

Action of p-*Nitrobenzyl Bromide on Sodium Salts of* β-*Aldoximes.*

The general method was to suspend the β-oxime in alcohol and add a solution of sodium ethoxide in alcohol (the oxime then dissolved as the sodium salt) followed by a warm solution of *p*-nitrobenzyl bromide in alcohol. The mixture was at once cooled in running water and then treated as described below.

β-*Benzaldoxime* (6 g. in 25 c.c.; 1·14 g. of sodium in 40 c.c.; 10·71 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After being kept for 24 hours, the solution was diluted with water and cooled in ice with stirring. The yellow solid thus obtained was washed with water, dried in the air, and crystallised three times from small quantities of benzene, giving *N*-*p*-nitrobenzylbenzaldoxime, m. p. 110° (Found : N, 11·3. Calc. : N, 10·9%) (compare Behrend and König, *loc. cit.*). No β-*O*-ether could be isolated from the benzene mother-liquors.

The *N*-ether (1 g. in 20 c.c. of benzene) was exposed to ultra-violet light for 54 hours and the solvent was then removed; the residue had a faint odour of benzaldehyde or benzonitrile and consisted practically entirely of unchanged *N*-ether (compare Brady and McHugh, J., 1924, **125**, 553).

N-*p*-Nitrobenzylbenzaldoxime (1 g.) and pure acetic anhydride (5 c.c.) were gently heated together. A somewhat vigorous reaction occurred at the boiling point, and the liquid was immediately cooled, poured into excess of 2*N*-sodium carbonate, and shaken for some time until the odour of the anhydride disappeared. The solid that separated, after being washed with water and crystallised from alcohol, was found to be benzo-*p*-nitrobenzylamide by comparison with an authentic specimen. This amide has been described by Hafner (*Ber.*, 1890, **23**, 339), but several improvements in the method of preparation have been devised. Phthal-*p*-nitrobenzylimide (0·5 g.), prepared from potassium phthalimide and *p*-nitrobenzyl bromide (Hammick and Locket, J., 1922, **121**, 2362; Salkowski, *Ber.*, 1889, **22**, 2142), was heated under reflux for 4 hours with 60% sulphuric acid (30 c.c.)—an improvement on Gabriel's method (*Ber.*, 1887, **20**, 2227). After cooling, the liquid was diluted with water, made alkaline with sodium hydroxide, and extracted with chloroform. The liquid *p*-nitrobenzylamine obtained on removal of the solvent was suspended in 2*N*-sodium hydroxide (30 c.c.) and shaken with benzoyl chloride (1 c.c.) for 30 minutes. The precipitated benzo-*p*-nitrobenzylamide was collected and crystallised from alcohol.

β-*o*-*Nitrobenzaldoxime* (4 g. in 25 c.c.; 0·56 g. of sodium in 30 c.c.; 5·2 g. of *p*-nitrobenzyl bromide in 50 c.c. of alcohol).—After 12 hours,

the yellow precipitate was collected, washed with a little alcohol, dried (yield, 3·7 g.; m. p. 170—175°), and extracted with warm ether; this removed 0·3 g. of material which, after crystallisation from alcohol, gave β-*O*-*p*-nitrobenzyl-*o*-nitrobenzaldoxime. The portion insoluble in ether, after three crystallisations from acetone, gave N-p-*nitrobenzyl*-o-*nitrobenzaldoxime* in long, pale yellow prisms, m. p. 203° (decomp.) (Found: N, 14·1. $C_{14}H_{11}O_5N_3$ requires N, 14·0%).

β-m-*Nitrobenzaldoxime* (7 g. in 30 c.c.; 0·97 g. of sodium in 50 c.c.; 9·11 g. of *p*-nitrobenzyl bromide in 120 c.c. of alcohol).—After 12 hours, the precipitate was collected, washed with alcohol and dried (yield, 12 g.; m. p. 215—218°). Crystallised from boiling glacial acetic acid, it gave N-p-*nitrobenzyl*-m-*nitrobenzaldoxime* in canary-yellow prisms, m. p. 223° (decomp.), which were very sparingly soluble in most organic solvents (Found: N, 14·2. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). The alcoholic filtrate from the *N*-ether was largely diluted with water and after 12 hours 0·6 g. of impure β-*O*-ether had separated (m. p. 90—103°). This was extracted with hot methyl alcohol, a little insoluble *N*-ether separated, and the filtrate cooled and diluted with water. The precipitated compound was pressed on a porous tile, washed with a little ether, and crystallised from methyl alcohol; pure β-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime was then obtained.

β-p-*Nitrobenzaldoxime* (5·42 g. in 60 c.c.; 0·75 g. of sodium in 30 c.c.; 7·05 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After 12 hours, the precipitate was washed with alcohol, dried (yield, 9·8 g.; m. p. 216—221°), and extracted with boiling acetone. The filtered extract was evaporated on the water-bath, leaving a solid residue. This was boiled with acetone, and the cooled, filtered solution was diluted with water, producing a precipitate which, crystallised from acetone and water and then twice from acetone, gave a very small quantity of β-*O*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime. The residue from the first acetone extraction, after crystallisation from boiling pyridine, gave *N*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime, m. p. 234—235° (decomp.). This compound was prepared by Behrend and König (*loc. cit.*) by the oxidation of *NN'*-di-*p*-nitrobenzylhydroxylamine. They give m. p. 227—228°, and we have found that this is the maximum melting point attainable if acetic acid or nitrobenzene, the solvents used by those authors, is employed for crystallisation.

β-3 : 4-*Methylenedioxybenzaldoxime* (3·3 g. in 40 c.c.; 0·46 g. of sodium in 30 c.c.; 4·32 g. of *p*-nitrobenzyl bromide in 60 c.c. of alcohol).—The solid was crystallised from acetone and water and then twice from acetone–alcohol, N-p-*nitrobenzyl*-3 : 4-*methylene*-

dioxybenzaldoxime being obtained in deep canary-yellow leaflets, m. p. 144° (Found: N, 9·3. $C_{15}H_{12}O_5N_2$ requires N, 9·3%). No β-*O*-ether could be isolated from the various mother-liquors.

β-p-*Methoxybenzaldoxime* (7·65 g. in 60 c.c.; 1·17 g. of sodium in 60 c.c.; 10·94 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After 24 hours, water (700 c.c.) was added to the mixture, and the precipitated solid was collected and air-dried (yield, 13·85 g.; m. p. 90—100°). After two crystallisations from acetone, N-p-*nitrobenzyl*-p-*methoxybenzaldoxime* was obtained in yellow needles, m. p. 150° (Found: N, 9·8. $C_{15}H_{14}O_4N_2$ requires N, 9·8%). The acetone mother-liquor from the first crop of crystals of the *N*-ether gave, on dilution, a further crop of *N*-ether. The aqueous-acetone filtrate was allowed to evaporate spontaneously and the solid obtained was extracted with boiling ether (100 c.c.), some *N*-ether remaining undissolved. Light petroleum (75 c.c.) was added to the solution; a sticky precipitate was then obtained which was rejected. The ether–light petroleum filtrate, on evaporation in a current of air, gave 0·9 g. of material which yielded, after crystallisation from methyl alcohol, β-*O*-*p*-nitrobenzyl-*p*-methoxybenzaldoxime.

β-3-*Nitro*-4-*methoxybenzaldoxime* (3·55 g. in 40 c.c.; 0·42 g. of sodium in 30 c.c.; 3·91 g. of *p*-nitrobenzyl bromide in 40 c.c. of alcohol).—After 12 hours, the yellow precipitate was collected (yield 6 g.) and crystallised twice from acetone, giving N-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime* in bright yellow needles, m. p. 232° (decomp.) (Found: N, 12·8. $C_{15}H_{13}O_6N_3$ requires N, 12·7%). The acetone mother-liquor from the first crystallisation was evaporated to dryness, and the residue extracted with boiling chloroform. The extract was separated from undissolved *N*-ether and evaporated to dryness; the residue (0·8 g.), after two crystallisations from alcohol–acetone, gave β-*O*-*p*-nitrobenzyl-3-nitro-4-methoxybenzaldoxime.

Hydrolysis of N-p-*Nitrobenzyl Ethers.*

N-*p*-Nitrobenzyl-*p*-methoxybenzaldoxime (4·3 g.) was triturated with 160 c.c. of concentrated hydrochloric acid; the mixture was then boiled under reflux for an hour, diluted with a little water, cooled, and extracted with chloroform. The extract, on evaporation, gave an oil which was identified as *p*-methoxybenzaldehyde by conversion into the semicarbazone, the yield of this compound being 2·8 g. (calc., 2·9 g.). The aqueous layer was evaporated to dryness on the water-bath; the *N*-*p*-nitrobenzylhydroxylamine hydrochloride that remained (yield, 2·7 g.; calc., 3·1 g.), on crystallisation from absolute alcohol by addition of ether, gave the pure compound, m. p. 179—181° (compare Behrend and König, *Annalen*, 1891, 263,

190). By addition of 2*N*-sodium carbonate to a concentrated aqueous solution of the hydrochloride, the free base was obtained, m. p. 120—122° after crystallisation from hot water (Behrend and König, *loc. cit.*). This method of preparing *N*-*p*-nitrobenzylhydroxylamine from *p*-methoxybenzaldoxime *N*-*p*-nitrobenzyl ether is preferable to that described by the above authors, since β-*p*-methoxybenzaldoxime is one of the easiest β-aldoximes to obtain pure and in quantity and the *N*-*p*-nitrobenzyl ether is more easily hydrolysed than that of *p*-nitrobenzaldoxime owing to the very sparing solubility of the latter.

The *N*-*p*-nitrobenzyl ethers of benzaldoxime, 3 : 4-methylenedioxy-, *o*-methoxy-, and 5-nitro-2-methoxy-benzaldoximes were hydrolysed in an analogous way; benzaldehyde and *o*-methoxybenzaldehyde were identified as semicarbazones and 3 : 4-methylenedioxy- and 5-nitro-2-methoxy-benzaldehydes as α-oximes.

N-*p*-Nitrobenzyl-*m*-nitrobenzaldoxime (8 g.) was triturated with 200 c.c. of boiling concentrated hydrochloric acid, and steam was rapidly passed through the mixture for 5 hours. The distillate on extraction with chloroform gave 3·9 g. of *m*-nitrobenzaldehyde (calc., 4·0 g.). The liquid in the flask on evaporation to dryness on the water-bath gave 5·2 g. of crude *N*-*p*-nitrobenzylhydroxylamine (calc., 5·4 g.), which was identified as before.

The *N*-*p*-nitrobenzyl ethers of *o*- and *p*-nitro- and 3-nitro-4-methoxy-benzaldoximes were hydrolysed similarly to the *m*-nitro-derivative. In the case of *N*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime, hydrobromic acid proved more satisfactory than hydrochloric acid. 3-Nitro-4-methoxybenzaldehyde was obtained as an oil and identified by conversion into the α-oxime.

Action of N-p-*Nitrobenzylhydroxylamine on Aldehydes.*

An alcoholic solution of the aldehyde was treated successively with alcoholic solutions of *N*-*p*-nitrobenzylhydroxylamine hydrochloride and potassium acetate, and the mixture kept for a definite time.

Cinnamaldehyde (1·9 g. in 4 c.c.; *N*-*p*-nitrobenzylhydroxylamine hydrochloride, 3·2 g., in 24 c.c.; potassium acetate, 2 g., in 20 c.c.). —After 12 hours, the precipitate was washed with a little alcohol and with water; 2·6 g. were then obtained. A further crop of 1·4 g. was obtained by diluting the mother-liquors.

N-p-*Nitrobenzylcinnamaldoxime* crystallises from benzene in lemon-yellow needles, m. p. 135° (Found: N, 9·9. $C_{16}H_{14}O_3N_2$ requires N, 9·9%). This compound could not be prepared by the action of *p*-nitrobenzyl bromide on the sodium salt of β-cinnamaldoxime, the products under various conditions being brown tars from

which nothing crystalline could be isolated. On hydrolysis with hydrochloric acid, the *N*-ether behaved abnormally, giving a yellow, crystalline substance mixed with a resinous material from which it could not be separated.

o-*Methoxybenzaldehyde* (0·5 g. in 5 c.c.; hydrochloride, 0·83 g., in 5 c.c.; acetate, 0·5 g., in 5 c.c. of alcohol).—0·72 G. of crude *N*-ether crystallised and a further 0·12 g. was obtained by diluting the mother-liquor. N-p-*Nitrobenzyl*-o-*methoxybenzaldoxime* crystallises from alcohol in very pale yellow, fern-like crystals, m. p. 141° (Found : N, 10·2. $C_{15}H_{14}O_4N_2$ requires N, 9·8%).

5-*Nitro*-2-*methoxybenzaldehyde* (2 g. in 25 c.c. of warm alcohol; hydrochloride, 2·3 g., in 20 c.c.; acetate, 1·4 g., in 20 c.c. of alcohol). —After being kept in cold water for an hour, the precipitate was collected and washed with water and with alcohol (yield 3·2 g.). N-p-*Nitrobenzyl*-5-*nitro*-2-*methoxybenzaldoxime* crystallises from nitrobenzene in yellow prisms, m. p. 237° (decomp.) (Found : N, 13·3. $C_{15}H_{13}O_6N_3$ requires N, 12·7%).

m-*Nitrobenzaldehyde* (0·37 g. in 5 c.c.; hydrochloride, 0·6 g., in 10 c.c.; acetate, 0·35 g., in 5 c.c.).—The reaction mixture was kept for 30 minutes and then diluted with water; an almost quantitative yield of *N*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime was obtained identical with that prepared from the sodium salt of the β-oxime. There was no indication of the formation of a second isomeride.

The System α-Benzaldoxime–p-Nitrobenzyl Bromide.

The α-benzaldoxime was crystallised from benzene and light petroleum; it melted in a capillary tube at 34° and froze in bulk at 32·9°. The *p*-nitrobenzyl bromide was crystallised first from light petroleum and then from alcohol; it melted in a capillary tube at 100° and froze in bulk at 97·9°. Cooling curves were constructed for mixtures of the two compounds in a vacuum-lagged silica vessel. It was found necessary to seed mixtures containing more than 87% of α-benzaldoxime with a crystal of α-benzaldoxime in order to induce crystallisation. The freezing points are given in Table III (*a* = molecular percentage of α-benzaldoxime).

TABLE III.

a.	F. p.	*a*.	F. p.	*a*.	F. p.	Eutectic.
0	97·9°	54·3	72·5°	85·6	37·8°	
4·3	96·1	61·1	67·7	88·9	27·8	27·2°
8·2	94·3	67·0	63·6	91·1	27·4	27·3
11·8	93·0	74·0	57·2	94·7	29·4	
18·1	89·2	78·1	51·7	97·3	30·8	
37·3	80·9	81·6	45·4	98·9	31·7	
47·2	76·5	83·6	41·2	100	32·9	

No indication of the formation of a compound was obtained. Equimolecular quantities of α-benzaldoxime and *p*-nitrobenzyl bromide dissolved in the minimum quantity of dry benzene were kept for 6 months. On removing the benzene, an oily solid was obtained which had the characteristic odour of α-benzaldoxime and, after being pressed on a porous tile, left a residue of *p*-nitrobenzyl bromide.

O-*Methyl Ethers of* m-*Nitrobenzaldoxime.*

Methoxyl Content and Molecular Weights.—The ethers employed were those prepared by Brady, Dunn, and Goldstein (J., 1926, 2398, 2402). α-*O*-Methyl-*m*-nitrobenzaldoxime has m. p. 63° (Found: OMe, 16·7; *M*, microcryoscopic in camphor, 181. Calc.: OMe, 17·2%; *M*, 180). β-*O*-Methyl-*m*-nitrobenzaldoxime has m. p. 75° (Found: OMe, 16·8%; *M*, microcryoscopic in camphor, 174).

Action of O-*Methylhydroxylamine on* m-*Nitrobenzaldehyde.*—The pure aldehyde (10 g.), dissolved in alcohol (150 c.c.), was mixed with *O*-methylhydroxylamine (3·3 g.) in alcohol (15 c.c.) and kept for 65 hours in a corked flask in the dark. The products were then precipitated in three fractions by very gradual addition of water with thorough stirring; in order to induce the third fraction to crystallise it was necessary to cool the mixture in ice. Fractions 1 and 2, constituting the bulk of the product (about 9 g.), were almost pure α-*O*-methyl-*m*-nitrobenzaldoxime (m. p. 63°). Fraction 3 (m. p. 42—44°) was redissolved in a small quantity of hot alcohol; from the cooled solution, more of the α-*O*-ether separated. The mother-liquor was cooled in ice and a little water added; a mixture then separated (m. p. 43—45°). After removal of this, further dilution followed by cooling in ice gave a product, m. p. 55—60°, which, after crystallisation from light petroleum, yielded a small quantity of nearly pure β-*O*-methyl-*m*-nitrobenzaldoxime, m. p. 70—71°; this melted at 73—74° and 45—50° when mixed with equal amounts of pure β-*O*-ether and α-*O*-ether, respectively. A similar result had previously been obtained by one of us using *O*-methylhydroxylamine hydrochloride, decomposed by sodium ethoxide in alcohol, and considerably smaller quantities of material.

Action of Ultra-violet Light on Some α-O-*Methyl Ethers.*

α-O-*Methyl*-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime.*—The ether was prepared by methylation of the oxime (Brady, Dunn, and Goldstein, *loc. cit.*). The same compound is formed when 6-nitro-3 : 4-methylenedioxybenzaldehyde (1 g.) in warm alcohol (40 c.c.) is mixed with a solution of *O*-methylhydroxylamine hydrochloride (0·5 g.) in a little water which has been treated with sodium ethoxide

in alcohol (0·14 g. of sodium in 25 c.c. of alcohol); after a few hours crystals of the α-*O*-ether separate. The α-*O*-ether (2·5 g.), dissolved in benzene (100 c.c.), was exposed in a quartz flask to ultra-violet light for 72 hours. A small amount of brown, flocculent precipitate was removed, the solution evaporated, and the residue, m. p. 99—104°, dissolved in warm acetone (40 c.c.). The cold solution was then fractionally precipitated with water. The first fraction was the α-*O*-ether (m. p. 147°). The second and third fractions (m. p. 100—105°) were combined and crystallised four times from alcohol; 0·2 g. of β-O-*methyl*-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime* was then obtained in long, straw-coloured needles, m. p. 122° (Found: N, 12·7. $C_9H_8O_5N_2$ requires N, 12·5%). A mixture of approximately equal quantities of the α- and β-*O*-ethers melted at 107—108°. The β-*O*-ether, when dissolved in chloroform and treated for a few seconds with hydrogen chloride, is converted into the α-*O*-ether, the solution on evaporation giving a product which melts at 146°, and at 147° when mixed with α-*O*-ether.

α-O-*Methyl*-3-*nitro*-4-*methoxybenzaldoxime*.—Similar treatment of this compound resulted in partial inversion, but the product (m. p. 103—104°) could not be separated into its components. When it was dissolved in chloroform and treated with hydrogen chloride, and the solution was evaporated to dryness, the mixture was reconverted into the α-ether.

In conclusion, we wish to thank the Government Grant Committee of the Royal Society for a grant towards the cost of a quartz-mercury lamp.

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CXXIX.—*The Isomerism of the Oximes. Part XXX. The Preparation of* o-*Methoxybenzaldoxime from Bisnitrosyl-*o-*methoxybenzyl.*

By OSCAR L. BRADY and CHARLES L. BENNETT.

THE preparation of the two isomeric forms of a substituted benzaldoxime is not always possible (Brady and Dunn, J., 1916, **109**, 666) and in no case is this more remarkable than in that of *o*-methoxybenzaldoxime, which exists only in the α-form, many attempts to obtain the isomeric β-compound through the hydrochloride in various ways, or by the action of light, having been completely unsuccessful (Brady and Dunn, J., 1923, **123**, 1787; Brady and McHugh, J., 1924, **125**, 584). For a summary of the facts bearing

on this problem, see Brady, Cosson, and Roper (J., 1925, **127**, 2427). An attempt has now been made to prepare β-*o*-methoxybenzaldoxime by the method by which Behrend and Nissen (*Annalen*, 1892, **269**, 390) first obtained β-*o*-chlorobenzaldoxime (compare also Behrend and König, *Annalen*, 1891, **263**, 216, 348). The latter compound has now been prepared from the α-oxime by the action of ultra-violet light (Brady and McHugh, *loc. cit.*) and through the hydrochloride by a special method (Brady, Cosson, and Roper, *loc. cit.*), but at the time of Behrend and Nissen's work the hydrochloride method had not been successfully applied (Dollfus, *Ber.*, 1892, **25**, 1923).

The method involves the preparation of N-o-*methoxybenzyl*-p-*methoxybenzaldoxime* (I) from *o*-methoxybenzyl chloride and β-*p*-methoxybenzaldoxime, its hydrolysis to N-o-*methoxybenzylhydroxylamine hydrochloride* (II), the conversion of this into *nitroso*-N-o-*methoxybenzylhydroxylamine* (III), which with a trace of nitric acid yields *bisnitrosyl*-o-*methoxybenzyl* (IV); the last compound, on treatment with alkali, gives *o*-methoxybenzaldoxime.

$$(o)\ MeO\cdot C_6H_4\cdot CH_2Cl + (p)\ MeO\cdot C_6H_4\cdot CH{:}NOH \longrightarrow$$
$$(I.)\ (p)\ MeO\cdot C_6H_4\cdot CH{:}N(:O)\cdot CH_2\cdot C_6H_4\cdot OMe\ (o) \longrightarrow$$
$$(II.)\ (o)\ MeO\cdot C_6H_4\cdot CH_2\cdot NH\cdot OH,HCl \longrightarrow$$
$$(III.)\ (o)\ MeO\cdot C_6H_4\cdot CH_2\cdot N(NO)\cdot OH \longrightarrow$$
$$(IV.)\ [(o)\ MeO\cdot C_6H_4\cdot CH_2\cdot NO]_2 \longrightarrow MeO\cdot C_6H_4\cdot CH{:}NOH$$

β-*p*-Methoxybenzaldoxime was chosen as the means of obtaining the *N*-ether, because this β-oxime is comparatively stable and is one of the easiest to prepare in the pure state. This method of obtaining the necessary *N*-substituted hydroxylamine was not used by Behrend and Nissen, but their method would have involved considerable loss of the valuable *o*-methoxybenzyl chloride.

Behrend and König, by decomposition of bisnitrosylbenzyl and of bisnitrosyl-*p*-nitrobenzyl, obtained approximately equal amounts of α- and β-benzaldoximes and α- and β-*p*-nitrobenzaldoximes, respectively, but it is difficult to say whether the α-oxime was a product of isomeric change of the β-oxime during the somewhat lengthy manipulations. If the structure of the bisnitrosyl compound adopted by Behrend be accepted (V) and the reaction be

$$(V.)\quad \begin{matrix} R\cdot CH_2\cdot N{-}O \\ \quad\quad\quad | \\ \quad\quad O{-}N\cdot CH_2R \end{matrix}$$

regarded as a depolymerisation followed by tautomeric change of the nitrosobenzyl, the formation of a mixture of the two isomerides might be expected. Unfortunately, although there is considerable evidence that the decomposition of bisnitrosyl-*o*-methoxybenzyl

leads to the formation of some β-methoxybenzaldoxime, it has not been possible to isolate enough of the β-oxime to identify it as thoroughly as could be desired.

EXPERIMENTAL.

N-o-*Methoxybenzyl*-p-*methoxybenzaldoxime* (I).—*o*-Methoxybenzyl chloride was prepared (1) by methylating saligenin with methyl iodide, methyl alcohol, and sodium methoxide, hydrolysing the product to *o*-methoxybenzyl alcohol, and converting this into the chloride with dry hydrogen chloride (Pschorr, Wolfes, and Buckow, *Ber.*, 1900, **33**, 165), (2) from *o*-methoxybenzaldehyde (from salicylaldehyde) by the Cannizzaro reaction.

A cold solution of β-*p*-methoxybenzaldoxime (10 g.) in the minimum quantity of absolute alcohol was treated with a cold solution of sodium (1·52 g.) in absolute alcohol and with an alcoholic solution of freshly distilled *o*-methoxybenzyl chloride (10 g.); a cloudiness appeared almost at once and heat was developed. After 12 hours, some of the *N*-ether had crystallised. Ice-cold water was added, and the crude *N*-ether separating was collected and dried over solid sodium hydroxide (yield, 95%). *o*-Methoxybenzyl chloride is readily hydrolysed by water, which must be excluded as completely as possible in the above preparation, otherwise the yield is much reduced. Crystallised from chloroform and light petroleum, N-o-*methoxybenzyl*-p-*methoxybenzaldoxime* formed colourless, monoclinic prisms, m. p. 123° (Found : N, 5·2. $C_{16}H_{17}O_3N$ requires N, 5·2%).

N-o-*Methoxybenzylhydroxylamine Hydrochloride* (II).—The crude *N*-ether obtained above was hydrolysed by boiling it under reflux for an hour with 20% hydrochloric acid; the *p*-methoxybenzaldehyde produced and any *O*-*o*-methoxybenzyl-*p*-methoxybenzaldoxime formed during methylation were then distilled in steam (*O*-ethers are not appreciably hydrolysed under these conditions). When the distillate no longer contained aldehyde, the hydrochloric acid solution remaining in the flask was evaporated on the water-bath until crystals appeared on the surface; on cooling, the greater part of the *N*-*o*-methoxybenzylhydroxylamine hydrochloride separated in crystals, usually tinged pink. Crystallised from absolute alcohol and dry ether, N-o-*methoxybenzylhydroxylamine hydrochloride* formed small, white needles, m. p. 136° (Found : N, 7·5; Cl, 18·6. $C_8H_{11}O_2N$,HCl requires N, 7·4; Cl, 18·7%). It is a powerful reducing agent, acting upon ferric chloride and Fehling's solution immediately at room temperature.

Nitroso-N-o-*methoxybenzylhydroxylamine* (III).—A 3% aqueous solution of the above hydrochloride was cooled in ice, and an

equivalent amount of sodium nitrite in the minimum amount of water added with stirring. After an hour the solution was thick with crystals, which were collected, washed with water, and air-dried (yield, 70%). Crystallised from chloroform and light petroleum, *nitroso*-N-o-*methoxybenzylhydroxylamine* was obtained in pale yellow, microscopic crystals, m. p. 73—74° (Found: N, 15·7. $C_8H_{10}O_3N_2$ requires N, 15·4%).

Bisnitrosyl-o-methoxybenzyl (IV).—*N-o*-Methoxybenzylhydroxylamine hydrochloride (5 g.) was dissolved in water (200 c.c.) and cooled in ice; a solution of hydrated sodium carbonate (4·2 g.) was added followed by glacial acetic acid (7·5 g.). Ether was poured on the mixture to form a layer, and an aqueous solution of potassium dichromate (2·66 g.) run in with vigorous stirring. After some time, the brown, flocculent, crystalline substance which had collected at the water–ether interface was removed, washed with a little ether, and dried (yield, 40—60%).

A much purer product was obtained by the following method. Nitroso-*N-o*-methoxybenzylhydroxylamine (5 g.) was dissolved in ether (60—70 c.c.), and glacial acetic acid (15 c.c.) was added together with one drop of fuming nitric acid. A steady stream of gas was evolved and after some time the sparingly soluble bisnitrosyl compound separated in 30—40% yield. After crystallising from chloroform and light petroleum, *bisnitrosyl-o-methoxybenzyl* was obtained in colourless needles, m. p. 125° (Found: N, 9·2. $C_{16}H_{18}O_4N_2$ requires N, 9·3%).

Action of Alkalis on Bisnitrosyl-o-methoxybenzyl.—Bisnitrosyl-o-methoxybenzyl was ground for some hours with 10% aqueous sodium hydroxide, cooling in ice. The undecomposed compound was filtered off, and a slight excess of an ice-cold, saturated solution of ammonium chloride added to the filtrate. The oxime, which was precipitated as an oil, was extracted with ether; on removal of the solvent, white crystals were obtained. These melted at 80—82°, and in admixture with α-*o*-methoxybenzaldoxime (m. p. 92°) at 59°. Under the microscope, they were seen to be a mixture of the characteristic long needles of the α-oxime and thin plates. Solution in alcohol and evaporation gave an oil which soon crystallised to the almost pure α-oxime, indicating that some unstable compound was present which changed rapidly to the α-oxime.

With 25% methyl-alcoholic potassium hydroxide, a more rapid decomposition of the bisnitrosyl compound occurred and the addition of ammonium chloride precipitated a compound, which melted alone at 80—85° and at 65° when mixed with the α-oxime. On crystallising it twice from acetone and water, a very small quantity

of a product, m. p. 101—102°, was obtained as compact, white prisms distinct from the slender crystals of the α-oxime. This appeared to be the β-oxime. It was very unstable and when after a few days an attempt was made to determine its configuration it was found that the m. p. had fallen to 92° and that the compound then consisted of the pure α-oxime. In subsequent preparations, using various methods of alkaline decomposition, we were never successful in obtaining this high-melting product again, but the low-melting, crude oxime always gave an orange-red coloration with alcoholic ferric chloride—a reaction characteristic of the β-aldoximes (Beck and Hase, *Annalen*, 1907, **355**, 29) and not given by α-*o*-methoxybenzaldoxime. Moreover, treatment of the crude product with acetic anhydride and then with sodium carbonate solution, extraction with ether, and hydrolysis of the oily product with sodium hydroxide resulted in the evolution of some ammonia. This indicated the presence of nitrile, probably formed from β-oxime in the crude product. The hydrolysis product was saturated with carbon dioxide and extracted with ether; the ether on evaporation gave α-*o*-methoxybenzaldoxime. The aqueous solution was acidified with dilute sulphuric acid and again extracted with ether; *o*-methoxybenzoic acid was then obtained. The ratio of oxime to acid was approximately 4 to 1. The difficulty encountered in obtaining the β-oxime by this method seems to be due to the slowness of the decomposition of the bisnitrosyl compound; owing to the instability of the β-oxime, most of it probably changes to the α-isomeride during manipulation; and fractional crystallisation of the product provides still further opportunity for the isomerisation to occur.

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CXXX.—*The Mechanism of the Reaction between a Carboxylic Ester and a Grignard Reagent.*

By DAVID RUNCIMAN BOYD and HAROLD HERBERT HATT.

FEW synthetic processes of organic chemistry have been more extensively used than that which leads to the formation of tertiary alcohols by the action of magnesium alkyl, or aryl, halides upon ethereal salts. The mechanism of the process, however, is still in some respects obscure. In his original papers dealing with this subject (*Compt. rend.*, 1901, **132**, 336; *Ann. Chim.*, 1901, **24**, 433), Grignard states that the reaction probably takes place in three stages:

(i) $R{\cdot}CO{\cdot}OEt \xrightarrow{R'{\cdot}MgBr} R{\cdot}CR'(OMgBr){\cdot}OEt.$

(ii) $R{\cdot}CR'(OMgBr){\cdot}OEt \xrightarrow{R'{\cdot}MgBr} R{\cdot}CR'_2{\cdot}OMgBr + EtO{\cdot}MgBr.$

(iii) $R{\cdot}CR'_2{\cdot}OMgBr \xrightarrow{H_2O} R{\cdot}CR'_2{\cdot}OH + HO{\cdot}MgBr.$

This scheme is reproduced in several well-known text-books.

An alternative view assumes that a ketone is formed as an intermediate product:

$$R{\cdot}CO{\cdot}OEt + R'{\cdot}MgBr = R{\cdot}CO{\cdot}R' + EtO{\cdot}MgBr;$$

and that the tertiary alcohol results from the action of the Grignard reagent upon the ketone. This mechanism was suggested by Reformatsky for the analogous case of an organo-zinc iodide reacting with an ethereal salt (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 881); it has been advocated by several writers, notably by Stadnikov (*Ber.*, 1914, **47**, 2133). Gomberg (*J. Amer. Chem. Soc.*, 1917, **39**, 2011) refers to Stadnikov's work as providing some evidence in support of the ketone hypothesis; but a consideration of Stadnikov's papers has led us to the conclusion that the evidence offered there is illusory.

Ketones have, it is true, been obtained by Blaise and Courtot (*Compt. rend.*, 1905, **140**, 370) by the action of water on the addition compounds which are formed on treating the esters of certain unsaturated acids with magnesium methyl iodide at 0°, *e.g.*,

$$CH_2{:}C(CH_3){\cdot}CO{\cdot}OEt \longrightarrow CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CO{\cdot}CH_3.$$

These results, however, are not out of harmony with Grignard's views. The appearance of a ketone amongst the products of the reaction may be attributed to the stability, under the conditions of the experiment, of the magnesium addition compound arising in stage (i) of the Grignard scheme. The experiments of Blaise and Courtot provide no evidence in support of the hypothesis that the formation of a ketone is a necessary step in the production of a tertiary alcohol. In order to establish the correctness of this view, it is necessary to show that the free ketone is present in the reaction mixture during the experiment. Such evidence we are now able to bring forward.

In connexion with investigations on derivatives of the triaryl carbinols, which have been in progress for some time, we have had frequent occasion to employ the Grignard reaction for the preparation of tertiary alcohols from ethereal salts, and in the course of this work we have found that if metallic magnesium is added to the reaction mixture the presence of a ketone is readily detected. When magnesium phenyl bromide, for example, was

allowed to react with ethyl *o*-toluate in the presence of metallic magnesium, the products of the reaction included diphenyldi-*o*-tolylpinacol (38%) in addition to diphenyl-*o*-tolylcarbinol (23%). The addition of the Grignard reagent to the ester and magnesium was invariably followed by the development of a deep red colour, which persisted, provided air was excluded, until the reaction mixture was treated with water.

The formation of pinacols under the conditions described is easily understood in the light of the observations of Couturier and Meunier, who found (*Bull. Soc. chim.*, 1905, **33**, 454) that magnesium amalgam reacts smoothly with acetone, giving an addition compound from which the corresponding pinacol is obtained on treatment with water:

$$2CH_3{\cdot}CO{\cdot}CH_3 + Mg = (CH_3)_2C(O)_2Mg(O)_2C(CH_3)_2$$

The more recent investigations of Schlenk (*Ber.*, 1911, **44**, 1182; 1913, **46**, 2840) have shown, further, that ketones combine with metallic sodium (or magnesium activated by iodine) to give intensely coloured metal ketyls, containing tervalent carbon, and that metallic pinacolates result from the union of two of these unsaturated molecules:

$$2\,\mathrm{R}\mathrm{R}'\!>\!\mathrm{C}(\mathrm{ONa})- \rightleftharpoons \mathrm{R}\mathrm{R}'\!>\!\mathrm{C}(\mathrm{ONa})-\mathrm{C}(\mathrm{ONa})<\!\mathrm{R}\mathrm{R}'$$

The phenomena observed in our experiments (production of pinacols and development of colour) are thus very simply explained if it is assumed that the ester reacts with the Grignard reagent to form a ketone and that some of the ketone escapes transformation to a tertiary alcohol by combining with metallic magnesium (activated by contact with the Grignard reagent): *

$$2\,\mathrm{R}\mathrm{R}'\!>\!\mathrm{C}{=}\mathrm{O} + Mg = \mathrm{R}\mathrm{R}'\!>\!\mathrm{C}(\mathrm{O})_2\mathrm{Mg}(\mathrm{O})_2\mathrm{C}<\!\mathrm{R}\mathrm{R}' \rightleftharpoons \mathrm{R}\mathrm{R}'\!>\!\mathrm{C}(\mathrm{O})_2\mathrm{Mg}(\mathrm{O})_2\mathrm{C}<\!\mathrm{R}\mathrm{R}'$$

* Since this work was completed a paper has been published by Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 236) in which it is shown that ketones are converted into pinacols by magnesium in the presence of a Grignard reagent or, more effectively, by treating the ketone with a mixture of magnesium and magnesium iodide. The activation of the magnesium in

Grignard's scheme, on the other hand, cannot be reconciled with the observed phenomena and must therefore be rejected in favour of the ketone hypothesis.

There remains the question, By what mechanism is the ketone produced from the ester? On theoretical grounds, it appears probable that the Grignard reagent and the ethereal salt react in the first place to give an additive compound, and that the ketone results from the decomposition of this primary complex. Some experimental evidence in support of this view is on record. Stadnikov (*loc. cit.*) found that benzhydryl acetate reacts, in the cold, with magnesium ethyl iodide to give an addition compound, from which the original ester can be recovered on treatment with water. Addition compounds of a somewhat similar character have been obtained from certain ketones (compare Klages, *Ber.*, 1902, **35**, 2633). Stadnikov explains his observations by postulating the formation of an oxonium compound:

$$R{-}CO{\cdot}OR' + R''{\cdot}MgBr = R{-}CO{\cdot}O{<}\begin{matrix}R'\\MgBr\\R''\end{matrix}.$$

The groups R′ and R″ in this complex are assumed by Stadnikov to be similarly situated, and the conclusion is drawn that two different ketones may result from its decomposition:

$$R{-}CO{\cdot}O{<}\begin{matrix}R'\\MgBr\\R''\end{matrix} \longrightarrow \begin{matrix}R{-}CO{\cdot}R'\\R{-}CO{\cdot}R''\end{matrix}$$

Stadnikov claims to have obtained experimental proof of the correctness of this hypothesis from the results of a study of the action of magnesium phenyl bromide upon (*a*) benzyl benzoate and (*b*) benzhydryl acetate.

The principal product of reaction (*a*) is triphenylcarbinol; but, in addition to this, Stadnikov isolated a small quantity of a substance, m. p. 72—73°, which he assumed to be triphenylethylene.

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both cases is attributed by Gomberg and Bachmann to the formation of a magnesous iodide:

(1) $Mg + MgI_2 \rightleftarrows 2Mg{-}I$.

(2) $Ph_2C{=}O + MgI = Ph_2C(OMgI){-}$.

(3) $2Ph_2C(OMgI){-} \rightleftarrows Ph_2C(OMgI){-}Ph_2C(OMgI){-} \longrightarrow Ph_2C(OH){-}Ph_2C(OH)$.

Very large yields of pinacols (92—99·6%) were obtained from eight ketones by Gomberg and Bachmann; and these authors have proved that the *simultaneous* action of both magnesium and magnesium iodide is demanded in the reduction of ketones.

of a product, m. p. 101—102°, was obtained as compact, white prisms distinct from the slender crystals of the α-oxime. This appeared to be the β-oxime. It was very unstable and when after a few days an attempt was made to determine its configuration it was found that the m. p. had fallen to 92° and that the compound then consisted of the pure α-oxime. In subsequent preparations, using various methods of alkaline decomposition, we were never successful in obtaining this high-melting product again, but the low-melting, crude oxime always gave an orange-red coloration with alcoholic ferric chloride—a reaction characteristic of the β-aldoximes (Beck and Hase, *Annalen*, 1907, **355**, 29) and not given by α-*o*-methoxybenzaldoxime. Moreover, treatment of the crude product with acetic anhydride and then with sodium carbonate solution, extraction with ether, and hydrolysis of the oily product with sodium hydroxide resulted in the evolution of some ammonia. This indicated the presence of nitrile, probably formed from β-oxime in the crude product. The hydrolysis product was saturated with carbon dioxide and extracted with ether; the ether on evaporation gave α-*o*-methoxybenzaldoxime. The aqueous solution was acidified with dilute sulphuric acid and again extracted with ether; *o*-methoxybenzoic acid was then obtained. The ratio of oxime to acid was approximately 4 to 1. The difficulty encountered in obtaining the β-oxime by this method seems to be due to the slowness of the decomposition of the bisnitrosyl compound; owing to the instability of the β-oxime, most of it probably changes to the α-isomeride during manipulation; and fractional crystallisation of the product provides still further opportunity for the isomerisation to occur.

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$$CH_2{:}C(CH_3){\cdot}CO{\cdot}OEt \longrightarrow CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CO{\cdot}CH_3.$$

These results, however, are not out of harmony with Grignard's views. The appearance of a ketone amongst the products of the reaction may be attributed to the stability, under the conditions of the experiment, of the magnesium addition compound arising in stage (i) of the Grignard scheme. The experiments of Blaise and Courtot provide no evidence in support of the hypothesis that the formation of a ketone is a necessary step in the production of a tertiary alcohol. In order to establish the correctness of this view, it is necessary to show that the free ketone is present in the reaction mixture during the experiment. Such evidence we are now able to bring forward.

In connexion with investigations on derivatives of the triaryl carbinols, which have been in progress for some time, we have had frequent occasion to employ the Grignard reaction for the preparation of tertiary alcohols from ethereal salts, and in the course of this work we have found that if metallic magnesium is added to the reaction mixture the presence of a ketone is readily detected. When magnesium phenyl bromide, for example, was

allowed to react with ethyl *o*-toluate in the presence of metallic magnesium, the products of the reaction included diphenyldi-*o*-tolylpinacol (38%) in addition to diphenyl-*o*-tolylcarbinol (23%). The addition of the Grignard reagent to the ester and magnesium was invariably followed by the development of a deep red colour, which persisted, provided air was excluded, until the reaction mixture was treated with water.

The formation of pinacols under the conditions described is easily understood in the light of the observations of Couturier and Meunier, who found (*Bull. Soc. chim.*, 1905, **33**, 454) that magnesium amalgam reacts smoothly with acetone, giving an addition compound from which the corresponding pinacol is obtained on treatment with water:

$$2CH_3{\cdot}CO{\cdot}CH_3 + Mg = (CH_3)_2C(O)_2Mg(O)_2C(CH_3)_2$$

The more recent investigations of Schlenk (*Ber.*, 1911, **44**, 1182; 1913, **46**, 2840) have shown, further, that ketones combine with metallic sodium (or magnesium activated by iodine) to give intensely coloured metal ketyls, containing tervalent carbon, and that metallic pinacolates result from the union of two of these unsaturated molecules:

$$2\ \begin{matrix}R\\R'\end{matrix}\!>\!C\!-\!ONa \rightleftharpoons \begin{matrix}R\\R'\end{matrix}\!>\!C(ONa)-C(ONa)<\!\begin{matrix}R\\R'\end{matrix}$$

The phenomena observed in our experiments (production of pinacols and development of colour) are thus very simply explained if it is assumed that the ester reacts with the Grignard reagent to form a ketone and that some of the ketone escapes transformation to a tertiary alcohol by combining with metallic magnesium (activated by contact with the Grignard reagent): *

$$2\ \begin{matrix}R\\R'\end{matrix}\!>\!C{=}O + Mg = \begin{matrix}R\\R'\end{matrix}\!>\!C(O)_2Mg(O)_2C<\!\begin{matrix}R\\R'\end{matrix} \rightleftharpoons \begin{matrix}R\\R'\end{matrix}\!>\!C(O)_2Mg(O)_2C<\!\begin{matrix}R\\R'\end{matrix}$$

* Since this work was completed a paper has been published by Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 236) in which it is shown that ketones are converted into pinacols by magnesium in the presence of a Grignard reagent or, more effectively, by treating the ketone with a mixture of magnesium and magnesium iodide. The activation of the magnesium in

Grignard's scheme, on the other hand, cannot be reconciled with the observed phenomena and must therefore be rejected in favour of the ketone hypothesis.

There remains the question, By what mechanism is the ketone produced from the ester? On theoretical grounds, it appears probable that the Grignard reagent and the ethereal salt react in the first place to give an additive compound, and that the ketone results from the decomposition of this primary complex. Some experimental evidence in support of this view is on record. Stadnikov (*loc. cit.*) found that benzhydryl acetate reacts, in the cold, with magnesium ethyl iodide to give an addition compound, from which the original ester can be recovered on treatment with water. Addition compounds of a somewhat similar character have been obtained from certain ketones (compare Klages, *Ber.*, 1902, **35**, 2633). Stadnikov explains his observations by postulating the formation of an oxonium compound :

$$R{-}CO{\cdot}OR' + R''{\cdot}MgBr = R{-}CO{\cdot}O\begin{matrix}R'\\ \diagup\\ MgBr\\ \diagdown\\ R''\end{matrix}.$$

The groups R′ and R″ in this complex are assumed by Stadnikov to be similarly situated, and the conclusion is drawn that two different ketones may result from its decomposition :

$$R{-}CO{\cdot}O\begin{matrix}R'\\ \diagup\\ MgBr\\ \diagdown\\ R''\end{matrix} \begin{matrix}\nearrow\ R{-}CO{\cdot}R'\\ \searrow\ R{-}CO{\cdot}R''\end{matrix}$$

Stadnikov claims to have obtained experimental proof of the correctness of this hypothesis from the results of a study of the action of magnesium phenyl bromide upon (*a*) benzyl benzoate and (*b*) benzhydryl acetate.

The principal product of reaction (*a*) is triphenylcarbinol; but, in addition to this, Stadnikov isolated a small quantity of a substance, m. p. 72—73°, which he assumed to be triphenylethylene.

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both cases is attributed by Gomberg and Bachmann to the formation of a magnesous iodide :

(1) $Mg + MgI_2 \rightleftarrows 2Mg{-}I$.

(2) $Ph_2C{=}O + MgI = Ph_2C(OMgI){-}$.

(3) $2Ph_2C(OMgI){-} \rightleftarrows Ph_2C(OMgI){-}Ph_2C(OMgI){-} \longrightarrow Ph_2C(OH){-}Ph_2C(OH){-}$

Very large yields of pinacols (92—99·6%) were obtained from eight ketones by Gomberg and Bachmann; and these authors have proved that the *simultaneous* action of both magnesium and magnesium iodide is demanded in the reduction of ketones.

On this assumption, he argues that phenyl benzyl ketone must have been formed as an intermediate product:

(i) $Ph{\cdot}CO{\cdot}O{\cdot}CH_2Ph + Ph{\cdot}MgBr = Ph{\cdot}CO{\cdot}O\langle \begin{matrix} Ph \\ MgBr \\ CH_2Ph \end{matrix}$

$= Ph{\cdot}CO{\cdot}CH_2Ph + Ph{\cdot}O{\cdot}MgBr$

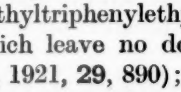
(ii) $Ph{\cdot}CO{\cdot}CH_2Ph + Ph{\cdot}MgBr = Ph_2C\langle \begin{matrix} O{\cdot}MgBr \\ CH_2Ph \end{matrix} \longrightarrow$

$Ph_2C(OH){\cdot}CH_2Ph \longrightarrow Ph_2C{:}CHPh$

No evidence is given in support of the formula $Ph_2C{:}CHPh$ except the analytical data: C, 93·34; H, 6·64%. These figures, however, are in excellent agreement with the composition of diphenyl (C, 93·46; H, 6·54%). The melting point given for the supposed triphenylethylene is the same as that of diphenyl, and the description of the crystalline form and solubility agrees with the assumption that the compound was diphenyl. On repeating Stadnikov's experiment we obtained the substance he describes, and identified it as diphenyl by the melting point of a mixture with an authentic specimen and by conversion into the dibromide.

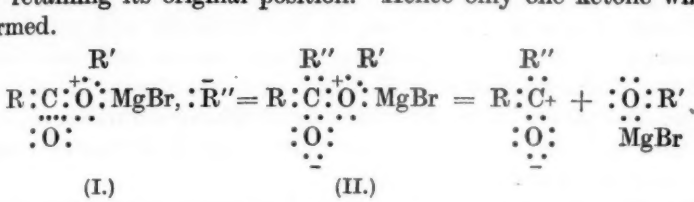
Amongst the products of reaction (*b*), Stadnikov obtained a hydrocarbon, m. p. 121—122°, which he assumed to be methyltriphenylethylene. The formation of the compound is explained as due to a series of changes similar to those given for case (*a*), and involving the production of benzhydryl methyl ketone as an intermediate step. Again, no evidence is brought forward in proof of the formula $CPh(CH_3){:}CPh_2$, except the analytical data. The figures given agree equally well with the compositions of several other substances,. Methyltriphenylethylene has recently been prepared by methods which leave no doubt as to its constitution (Levy, *Bull. Soc. chim.*, 1921, **29**, 890); it melts at 89—90°.

There is thus no experimental foundation for the view that an ester, R·CO·OR′, can react with a Grignard reagent, R″·MgBr, to give a ketone with the formula R·CO·R′. Hence Stadnikov's oxonium formula, in its original form, must be rejected, since it suggests possibilities of reaction which are not realised in practice. If, however, the Stadnikov formula is written in electronic fashion,



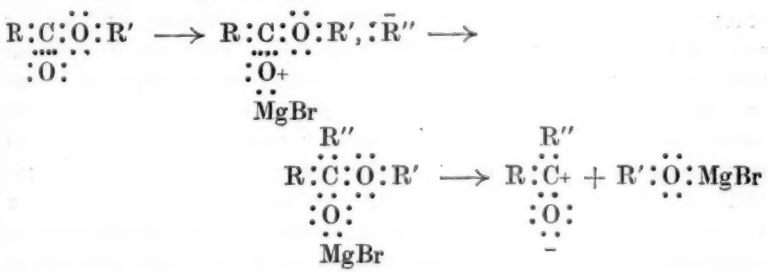
it becomes apparent that the groups R′ and R″ are not similarly situated. R″ is negatively charged and retained in the molecule by the electrostatic attraction of the positive oxonium oxygen atom; R′, on the other hand, is attached by a co-valency to the

oxygen. The rearrangement of the oxonium compound will naturally take place by a movement of the radical R″, the radical R′ retaining its original position. Hence only one ketone will be formed.

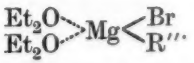


(I.) (II.)

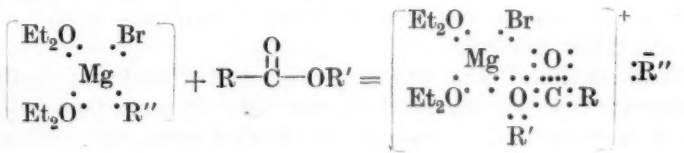
The magnesium complex (II) may be expected to break down with extreme ease, giving free ketone and the aryloxy-magnesium halide. The ketone thus liberated will be in a highly reactive form, and rapid combination with a Grignard reagent, or with activated magnesium, may be anticipated. This hypothesis appears to us to be the most satisfactory way of interpreting the phenomena. It is possible, however, that the formation of the primary addition compound may be due to the residual affinity of the carbonyl oxygen (compare v. Braun and Kirschbaum, *Ber.*, 1919, **52**, 1725, for the analogous case of a ketone addition compound), and not to that of the ethereal oxygen :



Either view can be combined with the interesting suggestions of Meisenheimer and Casper (*Ber.*, 1921, **54**, 1655), who regard the Grignard reagent as a magnesium complex compound containing two molecules of ether,



The primary reaction between this compound and an ethereal salt may be represented as follows :



Considered as a practical method for the preparation of pinacols, the new process presents advantages in certain cases, since it starts from the ester, which is usually more accessible than the ketone. Indirectly it provides a method for the synthesis of ketones and secondary alcohols, pinacols being readily decomposed into these products. The yield of pinacol, however, varies greatly in different cases. It appears to be dependent upon the constitutions of both the ester and the Grignard reagent: the study of the reaction from this point of view is being continued.

One other point of some practical importance may be noticed. In the preparation of triphenylcarbinol from magnesium phenyl bromide the crude carbinol is always associated with other compounds which lower its melting point and render its isolation in good yield less easy than might be expected. One of these compounds, diphenyl (invariably formed during the preparation of the Grignard reagent), is well known and easily removed. But the literature contains references to other by-products whose constitutions have not been elucidated. Schroeter, in an experiment on the preparation of triphenylcarbinol from carbon dioxide and magnesium phenyl bromide (*Ber.*, 1903, **36**, 3005), obtained a substance (A), m. p. 165°, which he suggests may be a molecular compound of triphenylcarbinol with benzophenone; and also a small quantity of a substance (B), m. p. 81°. From the description given of the properties of (A) there can be little doubt that it was an impure specimen of benzpinacol. As to the constitution of (B), Schroeter offers no opinion. A compound melting at about the same temperature (83—84°) was recently obtained by Stadnikov (*Ber.*, 1924, **57**, 1)] from methyl benzoate by prolonged boiling with a Grignard reagent prepared from bromobenzene. This compound was regarded by Stadnikov as the methyl ether of triphenylcarbinol, and an elaborate series of equations is given to account for its formation. We have repeated Stadnikov's experiment several times and have also tried various modifications of the conditions, but on no occasion have we detected the presence of the methyl ether of triphenylcarbinol amongst the products of the reaction between methyl benzoate and magnesium phenyl bromide.

We have, however, observed the occurrence of a small quantity of the *ethyl* ether of triphenylcarbinol as a by-product in the preparation of the carbinol from methyl benzoate and magnesium phenyl bromide in certain cases when ethyl alcohol was used as the crystallisation medium.

The methyl and ethyl ethers of triphenylcarbinol may easily be confused; their melting points do not differ by more than a degree (m. p. of methyl ether, 82°; m. p. of ethyl ether, 83°. Richter's

Lexikon), and their percentage compositions are almost identical. They can readily be distinguished by a mixed melting point determination, but Stadnikov makes no mention of such an observation. In the circumstances, we are of opinion that the compound, m. p. 83—84°, obtained by him from methyl benzoate was the ethyl ether of triphenylcarbinol and not, as he supposed, the methyl compound. Schroeter's substance, m. p. 81°, was, doubtless, also the ethyl ether of the carbinol.

Experimental.

In the preparation of the Grignard reagents, iodine was employed in small quantity to activate the magnesium.

The Action of Magnesium Phenyl Bromide on Ethyl o-*Toluate.*—Bistrzycki and Gyr (*Ber.*, 1904, **37**, 1248) obtained a 40% yield of diphenyl-*o*-tolylcarbinol from methyl *o*-toluate and magnesium phenyl bromide; they do not record the formation of any by-products. In our experiments, the ethyl ester was used.

Expt. 1. The product obtained on decomposing the magnesium complex with ice and dilute sulphuric acid was steam-distilled, and the residue crystallised from light petroleum and alcohol. The yield of carbinol, m. p. 98—98·5°, was 28·5%.

Expt. 2. 41 G. of the ester, dissolved in 60 c.c. of ether, were added to a Grignard reagent prepared from 13·5 g. of magnesium, 98 g. of bromobenzene and 200 c.c. of ether. In the hope of improving the yield, the procedure was modified as follows. After decomposition of the magnesium compound, the ethereal layer was removed, and the ether distilled off. On pouring the residual oil into alcohol, fine, white needles (A), m. p. 155°, immediately separated. Further small quantities of (A) were deposited from the solution on keeping, the total yield being 6·7 g. The residue left on evaporation of the alcoholic solution was steam-distilled, and the non-volatile portion crystallised from alcohol. In this way, 20·3 g. of diphenyl-*o*-tolylcarbinol were obtained. From the oil remaining after this crystallisation, 7·35 g. of diphenyl-*o*-tolylchloromethane were precipitated on passing hydrogen chloride gas through an ethereal solution containing fused calcium chloride.

The product (A), after several crystallisations from aqueous alcohol, melted at 160°. It crystallised well from benzene (needles, rapidly efflorescing in the air), or glacial acetic acid. It was identified as *diphenyldi-o-tolylpinacol* by analysis (C, 85·1; H, 6·9. $C_{28}H_{26}O_2$ requires C, 85·2; H, 6·65%) and by conversion into a mixture of phenyl-*o*-tolylcarbinol and phenyl *o*-tolyl ketone. Transformation into the secondary alcohol and ketone was brought

about either by heating for some hours at 120—125° or by treatment with hot alcoholic potash. On treatment with this reagent, it dissolved, imparting a characteristic, fleeting, deep-blue colour to the solution (compare Schlenk and Thal, *Ber.*, 1913, **46**, 2840). The oily product of the reaction, on being rubbed with light petroleum, gave crystals of phenyl-*o*-tolylcarbinol, identified by melting point (91·5°, after three crystallisations from ether–light petroleum) and by analysis (C, 84·9; H, 7·3. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%). The oil left after separation of the phenyl-*o*-tolylcarbinol boiled at 286—288°, and on treatment with alkaline-alcoholic hydroxylamine gave an oxime, m. p. 101·5—103·5° after crystallisation from aqueous alcohol. Smith (*Ber.*, 1891, **24**, 4046) gives 105° as the melting point of *anti*-phenyl-*o*-tolylketoxime.

The yields of pinacol and carbinol in this experiment were, respectively, 13·6% and 39·7%. Cohen, who prepared diphenyl-di-*o*-tolylpinacol by reduction of phenyl *o*-tolyl ketone (*Rec. trav. chim.*, 1919, **38**, 113), gives 163° as the melting point.

Expt. 3. The formation of pinacol in the preceding experiment was attributed to the presence in the reaction mixture of some metallic magnesium left over in the preparation of the Grignard reagent. This view was confirmed by removing any undissolved metal as completely as possible before allowing the reagent to mix with the ester. For this purpose, the Grignard reagent was filtered through an asbestos pad before entering the solution of ester (7·5 g.) in dry ether. The reaction product, after treatment in the usual way, was poured into alcohol, kept for 9 days, and inoculated with diphenyldi-*o*-tolylpinacol; 0·02 g. of product, m. p. 154°, was then obtained (equivalent to a yield of 0·26% of pinacol). On addition of light petroleum to the oily liquid, from which the pinacol had separated, diphenyl-*o*-tolylcarbinol (1·29 g.) crystallised; and the mother-liquor from this crystallisation, on long standing, deposited 0·77 g. of the *ethyl ether* of diphenyl-*o*-tolylcarbinol (large, colourless prisms, m. p. 96°), identified by the melting point of a mixture with a specimen prepared from diphenyl-*o*-tolylcarbinyl chloride (Found: OEt, 11·56. $C_{20}H_{17}OEt$ requires OEt, 14·9%).

Expt. 4. In order to obtain a maximum yield of pinacol, the reaction was carried out in the presence of a considerable excess of magnesium. The Grignard reagent, prepared from 16·2 g. of bromobenzene, 5 g. of magnesium, and 50 c.c. of dry ether, was filtered from the excess of magnesium, and the excess of metal was introduced into a solution of 7·5 g. of ethyl *o*-toluate in 30 c.c. of dry ether. The Grignard reagent was then added gradually (3 hours) to the ester solution, which was stirred and refluxed gently. Heating was continued for an hour after all the reagent had been added. All

these operations were carried out in an atmosphere of dry nitrogen. The reaction mixture remained throughout a deep red-orange colour. The product, treated in the usual way, gave 3·62 g. of pinacol (38%) and 2·92 g. of carbinol (23·3%).

The Action of Magnesium Phenyl Bromide on Methyl Benzoate.—In the following experiments, no attempt was made to exclude dry atmospheric oxygen.

Expt. 1. A Grignard reagent (prepared from 24·4 g. of bromobenzene, 7·5 g. of magnesium, and 70 c.c. of ether) was mixed with an ethereal solution of 20·9 g. of methyl benzoate, to which had been added the magnesium remaining over in the preparation of the magnesium phenyl bromide. The product was decomposed with ice and dilute sulphuric acid and extracted with ether. The semi-crystalline mass left on evaporation of the ether gave, on fractional crystallisation from ethyl alcohol, 8·7 g. (43·5%) of triphenylcarbinol (m. p. 160—161°) and 0·6 g. (2·2%) of benzpinacol, melting at 166—167° (m. p. after two crystallisations from aqueous alcohol, 185—186°). The benzpinacol was identified by conversion into benzhydrol (m. p. 67°) and benzophenoneoxime (m. p. 142—143°). The oil which did not crystallise in this treatment was steam-distilled. The steam distillate on fractional distillation yielded 10·08 g. of methyl benzoate, 0·3 g. of diphenyl, and 1·12 g. of residue. From the 1·12 g. of residue there resulted, on treatment with alkaline-alcoholic hydroxylamine, 0·46 g. of benzophenoneoxime, m. p. 142—143° after two crystallisations from aqueous alcohol (mixed m. p. 142—143°). The oil remaining after the steam distillation amounted to 2·55 g., and this when fractionally crystallised yielded, besides triphenylcarbinol, some colourless crystals melting between 70° and 78°. These, on recrystallisation from methyl alcohol, melted at 81—82°; they were identified as the ethyl ether of triphenylcarbinol. Mixed with a specimen of this ether (m. p. 80—82°), the crystals melted at 81·5°. A mixture of the substance with the methyl ether of triphenylcarbinol (m. p. 83—84°) melted at 60—63°, softening at 58°. A mixture of the methyl and ethyl ethers of triphenylcarbinol melted at 66—70°, softening at 53°.

Expt. 2. The Grignard reagent (prepared from 24·1 g. of bromobenzene, 4·5 g. of magnesium, and 70 c.c. of ether) was filtered and added slowly to an ethereal solution of 20·9 g. of methyl benzoate, containing 2·5 g. of magnesium turnings and a little metallic mercury. The reaction product, worked up in the usual way, yielded 2·15 g. (7·8%) of benzpinacol and 8·3 g. (41·5%) of triphenylcarbinol.

Expt. 3. Methyl benzoate (14 g.) was added fairly rapidly to a

Grignard reagent prepared from 34 g. of bromobenzene, 4·8 g. of magnesium, and 100 c.c. of ether. After the first reaction had ceased, the mixture was refluxed in a water-bath for 15 hours. The product was worked up as in Expt. 1, but the ethereal solution before evaporation was shaken with dilute aqueous sodium hydroxide in order to remove any free sulphuric acid. The following yields were obtained: triphenylcarbinol, 13·3 g. (49·7%); benzpinacol, 0·11 g.; and the ethyl ether of triphenylcarbinol, 1·62 g. (5·7%). The last compound was identified by a mixed melting point (83°), and conversion into the carbinol (mixed m. p. 160—161°) by treatment with concentrated sulphuric acid and glacial acetic acid.

The Action of Magnesium o-*Tolyl Bromide on Ethyl* o-*Toluate.*—The reaction was carried out exactly as described under Expt. 4 for the preparation of diphenyldi-*o*-tolylpinacol. The Grignard reagent was prepared from 16·5 g. of *o*-bromotoluene, 4·6 g. of magnesium, and 50 c.c. of ether; the undissolved magnesium being transferred to the solution of ethyl *o*-toluate (6·7 g.) in 30 c.c. of ether.

Immediately the Grignard reagent entered the ester solution, a deep reddish-violet colour was observed, which persisted until treatment of the reaction products with ice and dilute sulphuric acid. The ethereal layer on evaporation left an oil. From this residual oil, after rubbing with alcohol, a crystalline powder separated, m. p. 158° (yield 0·46 g.); and, on keeping, a further 0·02 g. of crystals (m. p. 148—153°) was obtained. This substance was very soluble in hot benzene, moderately easily soluble in alcohol, and insoluble in light petroleum. It was analysed after recrystallisation from benzene (Found: C, 85·2; H, 7·25. Calc. for $C_{30}H_{30}O_2$: C, 85·3; H, 7·2%). From its analysis, its decomposition on melting, and the evanescent deep green colour which it gives on dissolving in hot alcoholic sodium ethoxide, the substance is evidently *tetra*-o-*tolylpinacol*. The yield of pinacol was 5·2%.

The oil left after crystallisation of the pinacol was steam-distilled. From the distillate, 0·2 g. of a crystalline substance was obtained, melting, after crystallisation from aqueous alcohol, at 118—122°. The residue from the steam distillation was extracted with ether, and the ethereal solution was dried and evaporated. An oil was thus obtained which, on being rubbed with light petroleum containing a little ether, gave 0·51 g. of the same crystalline substance. After crystallisation from aqueous alcohol, it melted at 119—119·5°. A mixed melting-point determination showed that it was not di-*p*-tolyl. Analysis after recrystallisation pointed to *di*-o-*tolylcarbinol* (Found: C, 84·7; H, 7·7. $C_{15}H_{16}O$ requires C, 84·9;

H, 7·6%). The substance dissolved in concentrated sulphuric acid, giving a strong red colour. The di-*o*-tolylcarbinol may arise from hydrolysis of the pinacol by magnesium hydroxide during the decomposition of the reaction products with ice. Tri-*o*-tolylcarbinol has not, so far, been isolated, and the study of this reaction is being continued.

The Action of Magnesium Phenyl Bromide on Benzyl Benzoate (Stadnikov, *Ber.*, 1914, **47**, 2140).—Benzyl benzoate was prepared from benzoyl chloride and benzyl alcohol by a Schotten–Baumann reaction. It was purified by fractionating it twice under reduced pressure. The ester was brought into reaction with magnesium phenyl bromide, the same amounts of reagents and the same procedure being used as directed by Stadnikov (*loc. cit.*). In the main, the products of the reaction were those recorded by Stadnikov; thus we obtained 0·25 g. of benzoic acid and 29·1 g. of triphenylcarbinol. The steam distillate was separated into two fractions, as he directs, and from the first there were obtained 5·9 g. of bromobenzene (b. p. 146—147°), 6·8 g. of benzyl alcohol (b. p. 201—205°), and a small amount of a crystalline residue. From the second fraction, 6 g. of benzyl alcohol (b. p. 204—210°) were obtained, together with 0·89 g. of the crystalline material supposed to be triphenylethylene. This substance melted at 62—67°, and, after two crystallisations from aqueous ethyl alcohol, formed colourless plates, m. p. 70—71°. The yield of pure product was 0·57 g. (Stadnikov obtained 0·55 g.). Mixed with diphenyl (m. p. 69—69·5°), the substance melted at 69·5—70·5°.

It was brominated by dissolving 0·5 g. in 3 g. of carbon disulphide and adding 3 g. of bromine. After refluxing for 6 hours, the carbon disulphide was evaporated under reduced pressure, and the crystalline product washed with caustic soda solution, water, and alcohol (yield, 0·72 g.). After two crystallisations from benzene, it formed small, colourless needles, m. p. 164·5°.

4 : 4′-Dibromodiphenyl, prepared in precisely the same manner from 0·5 g. of diphenyl and crystallised twice from benzene, melted at 163—164°. For the mixed melting point, the value 163·5—164·5° was obtained.

Postscript.—Barnett, Cook, and Nixon (this vol., p. 504) have recorded the formation of *s*-*oo*′-dibenzylbenzpinacol as one of the products of the action of magnesium phenyl bromide on ethyl *o*-benzylbenzoate. The announcement of our results led these authors to repeat this experiment, and in a private communication they inform us that, in agreement with our observations, they obtained no pinacol when a filtered solution of magnesium phenyl bromide was employed.

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us (H. H. H.) to take part in this investigation.

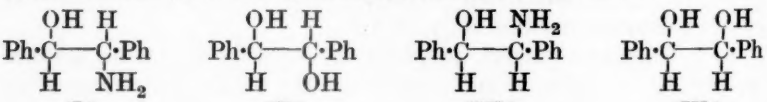
UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, February 12th*, 1927.]

CXXXI.—*The Optically Active Diphenylhydroxyethylamines and* iso*Hydrobenzoins. Part I.*

By JOHN READ and CATHERINE CASSELS STEELE.

THE constitution, $OH{\cdot}CHPh{\cdot}CHPh{\cdot}NH_2$, assigned to the diphenylhydroxyethylamines contains two dissimilar asymmetric carbon atoms and thus demands two externally compensated and four optically active stereoisomerides. A mixture of the two externally compensated bases is produced (i) in the reduction of benzoinoxime with sodium amalgam (Söderbaum, *Ber.*, 1895, **28**, 2523), and (ii) in the condensation of benzaldehyde and glycine (Erlenmeyer, *Annalen*, 1899, **307**, 97), diphenylhydroxyethylamine (m. p. 163°) predominating in the first reaction and *iso*diphenylhydroxyethylamine (m. p. 129—130°) in the second. Only the *iso*-base appears to have been resolved into optically active components (*Annalen*, 1904, **337**, 321; compare *Ber.*, 1899, **32**, 2378).

The base of m. p. 129—130° was originally regarded as *iso*diphenylhydroxyethylamine (I) by Erlenmeyer (*Annalen*, 1899, **307**, 97) because of its conversion by nitrous acid into *iso*hydrobenzoin; the latter substance, owing to its resolution into optically active components (*vide infra*), was assigned configuration (II). According to this scheme, diphenylhydroxyethylamine (m. p. 163°) would correspond configurationally to internally compensated hydrobenzoin (IV), thus possessing configuration (III):



(I.) (II.) (III.) (IV.)

It was found later, however, that both of the externally compensated bases gave a mixture of *iso*hydrobenzoin and hydrobenzoin in this reaction, the former product predominating in each instance (*Annalen*, 1899, **307**, 130, 136). Erlenmeyer was in consequence led to postulate the intermediate formation of a diazo-compound, $Ph{\cdot}CH(OH){\cdot}C(:N_2){\cdot}Ph$, containing only one asymmetric carbon atom in the molecule. The mechanism of the reaction has been discussed more recently by McKenzie and Richardson (J., 1923, **123**, 82).

We now describe the optical resolution of *dl*-diphenylhydroxyethylamine with *d*-oxymethylenecamphor and also with *d*-camphorsulphonic acid; the base appears to form a partly racemic salt with *d*-α-bromocamphorsulphonic acid. The optical rotatory powers of the two stereoisomeric bases show some remarkable contrasts: the respective values of $[\alpha]_D$ for *d*-diphenylhydroxyethylamine, *d*-diphenylhydroxyethylamine hydrochloride, and benzylidene-*d*-diphenylhydroxyethylamine were + 10·0° (alcohol), + 69·3° (water), and − 81·4° (alcohol); the corresponding values observed by us for the *d-iso*-base and its hydrochloride were + 125·0° and + 81·7°, whilst benzylidene-*d-iso*diphenylhydroxyethylamine gave $[\alpha]_D$ + 56·0° (*Annalen*, 1904, **337**, 343). *d*-Diphenylhydroxyethylamine showed a strong mutarotation in acetone, $[\alpha]_D$ changing from + 15·1° to − 108·8° in 90 minutes; the corresponding change for the *l-iso*-base was from − 102·2° to − 90·3°; in this respect, the *iso*-base thus appears to provide the closer analogy to the constitutionally similar hydroxyhydrindamine, the optically active forms of which show a weak but distinct mutarotation in acetone (J., 1912, **101**, 769).

Upon treatment with nitrous acid, *dl*-diphenylhydroxyethylamine gave a mixture containing hydrobenzoin, *dl-iso*hydrobenzoin, and probably deoxybenzoin; the crude products obtained similarly from *l*-diphenylhydroxyethylamine, *l-iso*diphenylhydroxyethylamine and *d-iso*diphenylhydroxyethylamine had $[\alpha]_D$ + 38·9°, − 47·1°, and + 49·7°, respectively, in alcohol. When fractionally crystallised, these optically active preparations yielded pure *d*- or *l-iso*-hydrobenzoin, having m. p. 146° and $[\alpha]_D \pm 90°$ approximately. The broad quantitative resemblance between the rotatory powers of the three crude products accords with Erlenmeyer's suggestion of the intermediate formation of a diazo-compound, but the results may be held alternatively to denote the occurrence of a Walden inversion affecting the enantiomorphously disposed groups ·CH(NH_2)Ph of formulæ (I) and (III), the same equilibrium being reached from the two sides. The oily material formed in the reactions may contain diphenylacetaldehyde, produced as a result of concomitant semipinacolinic deamination (compare McKenzie and Roger, J., 1924, **125**, 844). Since *l*-diphenylhydroxyethylamine and *d-iso*diphenylhydroxyethylamine both yield *d-iso*hydrobenzoin, it may be inferred that the group Ph·CH(OH)· has a similar spatial disposition in the molecules of these two bases: for example, if formula (I) is *d-iso*diphenylhydroxyethylamine, (III) is *l*-diphenylhydroxyethylamine. It appears that the optically active *iso*hydrobenzoins are less soluble than either *dl-iso*hydrobenzoin or hydrobenzoin.

The reaction with nitrous acid thus affords no decisive evidence

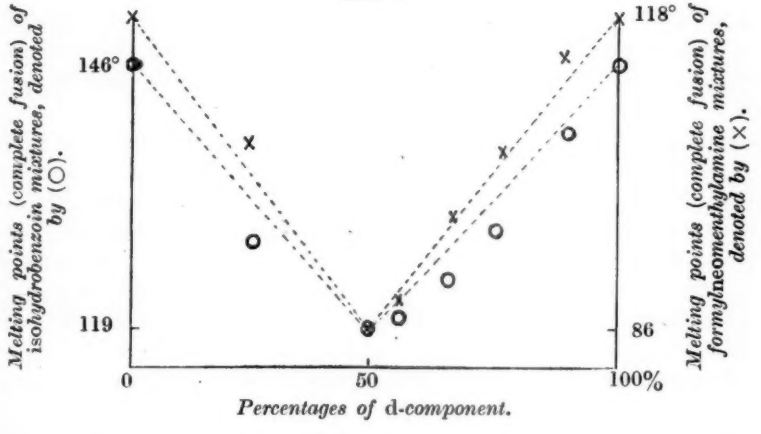
concerning the molecular configurations of the stereoisomeric bases. We suggest, however, that diphenylhydroxyethylamine probably possesses the more symmetric configuration (III), on account of (*a*) the low rotatory power of the free base, (*b*) the remarkable change in rotatory power upon annulling the electropositive influence of the amino-group, and (*c*) the comparative ease with which this base yields condensation products containing heterocyclic ring-systems (compare *Ber.*, 1896, **29**, 1210; *Annalen*, 1904, **337**, 352). The *iso*-base would thus correspond to configuration (I), as suggested by Erlenmeyer on grounds which are no longer tenable (*vide supra*).

Bodewig (*Annalen*, 1876, **182**, 279) found that the crystals separating from ethereal solutions of optically inactive *iso*hydrobenzoin were hemihedral, and by means of a mechanical separation of *d*- and *l*-crystals Erlenmeyer (*Ber.*, 1897, **30**, 1531) obtained specimens exhibiting optical activity in alcoholic solution. The polarimetric data are not precise, and no melting points are quoted, but apparently the maximum rotation observed was $[\alpha]_D$ — 7·30°. Since we now record maximum values of $[\alpha]_D$ + 90·5° and — 89·7° for *d*- and *l*-*iso*hydrobenzoin, respectively, it appears that the selected crystals contained not more than 54% of the *l*-component. The fission of *dl*-*iso*hydrobenzoin into optically active components by Erlenmeyer has been accepted for thirty years as a standard example of optical resolution by Pasteur's first method of so-called "spontaneous separation of enantiomers" (compare A. Werner, "Lehrbuch der Stereochemie," 1904, p. 62). It now appears that the formation of well-defined enantiomorphous crystals is not necessarily indicative of a complete optical resolution by this method. The melting-point curve of mixtures of *d*- and *l*-*iso*hydrobenzoin (Fig. 1) departs so markedly from the rectilinear form, when the temperatures of complete fusion are plotted, as to be incompatible with the existence of a conglomerate; the curve conforms, in fact, to Roozeboom's Fig. 11 (*Z. physikal. Chem.*, 1899, **28**, 510), thus indicating the formation of mixed crystals.

It is thus shown that mixed crystals derived from externally compensated organic substances may crystallise in enantiomorphously developed forms. In the light of these observations, it now seems justifiable to advance formyl-*dl*-*neo*menthylamine as a second example of the kind. This substance also yields *d*- and *l*-oriented crystals with hemihedral facets, which, again, display only a slight optical activity in solution; whilst pure formyl-*d*-*neo*menthylamine exhibits no hemihedry (J., 1926, 2228, 2219). Although in this case the melting-point curve (Fig. 1) does not depart so markedly from the conglomerate type as the above-

mentioned curve, yet a certain similarity to Roozeboom's Fig. 11 is manifest; moreover, it is clear that a crystal containing a slight excess of one enantiomeride exhibits hemihedral facets, whilst crystals of the pure optically active forms do not. Consequently, if formyl-*dl-neo*menthylamine deposited a conglomerate of crystals of the pure *d*- and *l*-forms, these crystals would be holohedral and crystallographically identical; since this is not so, the hemihedral crystals which are actually deposited must be regarded as mixed crystals rather than as a conglomerate. When sufficient material becomes available, it will thus be of particular interest to secure a crystallographic examination of pure *d*- and *l-iso*hydrobenzoin, which may also prove to be holohedral. Meanwhile, it becomes

FIG. 1.



necessary to revise the opinions which have hitherto prevailed concerning the applicability of Pasteur's method of optical resolution by the mechanical separation of *d*- and *l*-oriented crystals.

EXPERIMENTAL.

Optical Resolution of dl-*Diphenylhydroxyethylamine by Condensation with* d-*Oxymethylenecamphor.*—The *dl*-base (m. p. 163°) was prepared from benzoinoxime by the method of Goldschmidt and Polonowska (*Ber.*, 1887, **20**, 492). An oily separation of the condensation product occurred almost at once upon mixing equivalent weights of the base and *d*-oxymethylenecamphor, dissolved, respectively, in warm 50% acetic acid and methylated spirit. After the mixture had been kept for 10 minutes on the water-bath, the product was isolated and freed from unchanged material in the usual way (J., 1913, **103**, 1516). The resulting viscid syrup crystal-

lised partly when kept in a desiccator; in absolute alcohol ($c = 1{\cdot}2$) it had $[\alpha]_D + 143°$. After three recrystallisations from ether–light petroleum, the solid portion yielded pure d-*diphenylhydroxyethylamino*-d-*methylenecamphor*, consisting of small, colourless prisms, m. p. 146°, $[\alpha]_D + 235°$. The oily fractions furnished by the mother-liquors consisted of somewhat impure *l*-diphenylhydroxyethylamino-*d*-methylenecamphor, and gave values of $[\alpha]_D$ ranging from $+ 99{\cdot}5°$ to $+ 101{\cdot}5°$.

When dissolved in rectified spirit and titrated with bromine (1 mol.), *d*-diphenylhydroxyethylamino-*d*-methylenecamphor readily yielded the hydrobromide of the corresponding *d*-base (J., 1913, **103**, 448). After evaporation to small bulk on the water-bath, the product was shaken with water and benzene: the aqueous layer deposited d-*diphenylhydroxyethylamine hydrobromide* upon evaporation to dryness. This salt crystallises from acetone in long, transparent needles, m. p. 192°, $[\alpha]_D + 59{\cdot}0°$, $[M]_D + 173°$ in aqueous solution ($c = 0{\cdot}5$) (Found: Br, 26·9. $C_{14}H_{15}ON,HBr$ requires Br, 27·2%).

d-*Diphenylhydroxyethylamine*, obtained by precipitating an aqueous solution of the hydrobromide with dilute ammonia, melted at 143° and had $[\alpha]_D + 10{\cdot}0°$, when dissolved in absolute alcohol ($c = 0{\cdot}65$). No mutarotation was noticed in absolute alcohol, but in acetone ($c = 0{\cdot}2$) the original value, $[\alpha]_D + 15{\cdot}1°$, changed to $- 108{\cdot}8°$ in 1·5 hours, and attained the constant value, $- 120{\cdot}8°$, in 6 hours. That the low optical rotation of the free base was not due to partial racemisation was shown by the fact that the *hydrochloride* prepared from it had $[\alpha]_D + 69{\cdot}3°$, $[M]_D + 173°$, in aqueous solution ($c = 0{\cdot}65$).

Benzylidene-d-*diphenylhydroxyethylamine* crystallises from aqueous alcohol in colourless, transparent prisms, m. p. 109°, $[\alpha]_D - 81{\cdot}4°$ in absolute alcohol ($c = 0{\cdot}5$).

When dissolved in rectified spirit and titrated with bromine, crude *l*-diphenylhydroxyethylamino-*d*-methylenecamphor, having $[\alpha]_D + 101{\cdot}5°$, yielded a lævorotatory salt, which after three recrystallisations from acetone gave a specimen of pure l-*diphenylhydroxyethylamine hydrobromide*, m. p. 192°, $[\alpha]_D - 59{\cdot}0°$, $[M]_D - 173°$, in aqueous solution ($c = 0{\cdot}65$).

dl-*Diphenylhydroxyethylamine hydrobromide*, prepared for comparison, crystallised from acetone in small needles, m. p. 184°; it is considerably more soluble than the optically active components.

Benzylidene-dl-*diphenylhydroxyethylamine* separates from ether–light petroleum in long, fine, translucent needles, m. p. 120·5°.

Crystallisation of dl-*Diphenylhydroxyethylamine with Optically Active Acids.*—1. Hot aqueous solutions of the hydrochloride of the

dl-base (2 mols.) and ammonium *d*-bromocamphorsulphonate (1 mol.) were mixed and allowed to cool. The resulting glistening plates, m. p. 210° (decomp.), appeared to consist of dl-*diphenylhydroxyethylamine* d-*bromocamphorsulphonate* (Found: *M*, by titration, 525. $C_{24}H_{30}O_5NBrS$ requires *M*, 524). The salt was obtained in almost quantitative yield, and the original separations showed values of $[M]_D$ ranging from about + 330° to + 350° in dilute aqueous solution (0·1264 g., made up to 20 c.c., gave α_D + 0·84°, $[\alpha]_D$ + 66·5°, $[M]_D$ + 348°). After one or two recrystallisations from aqueous alcohol, the molecular rotation fell to $[M]_D$ + 273° (0·1018 g., made up to 20 c.c., gave α_D + 0·53°, $[\alpha]_D$ + 52·1°); this value, which is practically coincident with that of the acid ion in dilute aqueous solution (J., 1910, **97**, 2201), was unaffected by further recrystallisation. Specimens of the base liberated from fractions of this salt, and also from the original aqueous filtrate, exhibited no appreciable optical rotation when dissolved in absolute alcohol (0·13 g. in 20 c.c.) and examined in a 2-dcm. tube. The variations in the rotatory power of the *d*-bromocamphorsulphonate thus appear to be attributable to tautomerism on the part of the acid (compare J., 1914, **105**, 800).

2. When evaporated to dryness on the water-bath, an alcoholic solution of equivalent weights of *dl*-diphenylhydroxyethylamine and *d*-camphorsulphonic acid yielded a colourless, crystalline solid. The crude product melted indefinitely at about 190°, and had $[\alpha]_D$ +17·8° in dilute aqueous solution; separations consisting of small prisms were readily deposited from solutions in acetone or chloroform. Five successive recrystallisations from these solvents furnished a pure specimen of d-*diphenylhydroxyethylamine* d-*camphorsulphonate*, m. p. 193°; 0·1213 g., made up to 20 c.c. with water, gave α_D + 0·62°, $[\alpha]_D$ + 51·5°, $[M]_D$ + 227° (Found: *M*, by titration, 447. $C_{24}H_{31}O_5NS$ requires *M*, 445). The calculated molecular rotatory power for the basic ion is thus + 175°, a value which is in excellent agreement with $[M]_D$ + 173°, recorded above for the hydrobromide of the *d*-base. In accordance with this conclusion, specimens of the free base and of the hydrobromide, prepared from the salt *dAdB*, gave optical rotations practically identical with those already recorded.

Owing to its pronounced solubility, the pure diastereoisomeric salt, *dAlB*, could not be isolated. An impure fraction, having $[M]_D$ + 38°, yielded a specimen of crude *l*-diphenylhydroxyethylamine hydrochloride having $[M]_D$ − 13°; this value is practically identical with the calculated value for the basic ion of the fraction in question, and thus it appears that both diastereoisomerides give the normal rotatory powers in dilute aqueous solution.

Action of Nitrous Acid on dl- *and* l-*Diphenylhydroxyethylamine.*—1. A dilute ice-cooled aqueous solution of *dl*-diphenylhydroxyethylamine hydrochloride was treated with the calculated amount of sodium nitrite solution, the reaction being completed on the water-bath. By repeated fractional crystallisation of the partly crystalline product from ether, fractions were isolated which melted at 134° and 118°, and appeared to consist of hydrobenzoin (m. p. 138°) and *iso*hydrobenzoin (m. p. 119°), respectively.

2. *l*-Diphenylhydroxyethylamine hydrobromide upon similar treatment yielded a partly crystalline product, which was extracted with ether and examined polarimetrically in absolute alcohol: 0·2366 g. in 20 c.c. gave α_D + 0·92°, $[\alpha]_D$ + 38·9°. The crude product was purified by recrystallisation from light petroleum; the first fraction melted indefinitely between 117° and 130°, and had $[\alpha]_D$ + 41·9° in absolute alcohol.

Action of Nitrous Acid on l- *and* d-iso*Diphenylhydroxyethylamine.*—1. *dl-iso*Diphenylhydroxyethylamine (*Annalen*, 1899, **307**, 120) upon resolution with *d*-tartaric acid (*Annalen*, 1904, **337**, 321) gave a separation which after one recrystallisation from boiling water consisted of l-iso*diphenylhydroxyethylamine hydrogen* d-*tartrate*, m. p. 177°, $[\alpha]_D$ − 42·6°, $[M]_D$ − 155°, in water (c = 0·5). l-iso-*Diphenylhydroxyethylamine*, m. p. 115°, obtained from this salt by precipitation with aqueous ammonia, gave $[\alpha]_D$ − 125·0° in absolute alcohol * (c = 0·65), no mutarotation being observed. In acetone solution (c = 0·6), a slight mutarotation occurred, the original value, $[\alpha]_D$ − 102·2°, changing to − 90·3° in 3 hours. The *hydrochloride* had $[\alpha]_D$ − 81·7°, $[M]_D$ − 204°, in aqueous solution (c = 0·65).

When treated with nitrous acid in the cold, as described above, *l-iso*diphenylhydroxyethylamine hydrochloride yielded a partly crystalline product having $[\alpha]_D$ − 47·1° in absolute alcohol (c = 1·05). A wholly crystalline fraction from ether–light petroleum had m. p. 114—125°, $[\alpha]_D$ − 48·0°; a final purification from hot alcohol yielded a crystalline separation having m. p. 138—142°, $[\alpha]_D$ − 79·7°.

In a further experiment, carried out at 70° instead of at 0°, a slight excess of sodium nitrite solution was added gradually to *l-iso*diphenylhydroxyethylamine hydrochloride in a dilute aqueous solution containing one equivalent of free hydrochloric acid. Upon cooling, the product consisted of a brown oil, together with a less amount of small, glistening needles having $[\alpha]_D$ − 80·7° in absolute

* Erlenmeyer (*loc. cit.*), using either *d*-tartaric acid or helicin as the resolving agent, observed $[\alpha]_D$ ±109·7°; by using *d*-camphorsulphonic acid, values of $[\alpha]_D$ as high as + 130° for the free base have been observed in this laboratory.

alcohol ($c = 0{\cdot}65$), m. p. 137—138°. After recrystallisation from ether–light petroleum, the needles gave $[\alpha]_D$ — 89·1°, m. p. 144°. A final recrystallisation from absolute alcohol yielded small, transparent prisms or leaflets, m. p. 146°, $[\alpha]_D$ — 89·7°; these appeared to consist of l-iso*hydrobenzoin* (Found: C, 78·4; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%). A mixture of this substance with the crystals melting at 138—142°, mentioned above, melted at 138—142°.

2. The crude *d-iso*diphenylhydroxyethylamine obtained by adding ammonia to the mother-liquors from the above resolution with *d*-tartaric acid, when crystallised from aqueous alcohol yielded a final (fourth) small fraction having $[\alpha]_D$ + 125·5° (absolute alcohol); the preceding fractions consisted of the optically impure *d-iso*-base. More of this base was prepared by mixing sodium *l*-tartrate (1 mol.), hydrochloric acid (1 mol.), and *dl-iso*diphenylhydroxyethylamine hydrochloride (2 mols.) in an appropriate quantity of hot water. The ensuing crystalline separation, when recrystallised from hot water, had $[\alpha]_D$ + 43·4° in dilute aqueous solution, and thus consisted of d-iso*diphenylhydroxyethylamine hydrogen* l-*tartrate*, m. p. 177°. The corresponding base had $[\alpha]_D$ + 125·5° (absolute alcohol).

Upon treating *d-iso*diphenylhydroxyethylamine with nitrous acid in the usual way at 0°, the resulting partly crystalline product had $[\alpha]_D$ + 49·7° in absolute alcohol. In preparing pure *d-iso*hydrobenzoin, it was found advantageous, in a further experiment, to add two equivalents of *N*-hydrochloric acid to the reaction mixture before heating on the water-bath to expel the nitrogen. The crystalline deposit formed upon cooling the liquid (0·7 g. from 5·5 g. of base) was readily separated from the accompanying oil: it had $[\alpha]_D$ + 77·0° (absolute alcohol), m. p. 135—139°. Recrystallisation from absolute alcohol yielded small, glistening prisms or leaflets of d-iso*hydrobenzoin*, m. p. 146°, $[\alpha]_D$ + 90·5° in absolute alcohol ($c = 0{\cdot}65$). In view of the sharp melting point and the close agreement of these values with the corresponding data for *l-iso*hydrobenzoin, the preparations may be regarded as optically pure.

Melting-point Curve of Mixtures of d- *and* l-iso*Hydrobenzoin.*—Solid mixtures of known composition were made by mixing and evaporating measured volumes of standard alcoholic solutions of the two components. The equimolecular mixture had a sharp melting point (119°). With the single exception indicated below, the other mixtures melted over a range of at least 5°, and the recorded temperature is that of complete fusion. In all instances, the result was checked by remelting the mixture after it had solidified. The melting points were as follows for mixtures con-

taining the stated percentages of the *d*-enantiomeride: 100, 146°; 90, 139°; 75, 129°; 65, 124°; 55, 119—120°; 50, 119°; 25, 128°. The melting point of pure *dl-iso*hydrobenzoin must thus be accepted as 119°; the values quoted in the literature range from 119° to 122°.

We express our indebtedness to the Department of Scientific and Industrial Research for a maintenance grant to one of the authors (C. C. S.). The research is being continued.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, March 2nd*, 1927.]

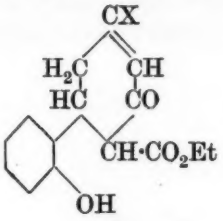
CXXXII.—*The Interaction of Ethyl Acetoacetate with Distyryl Ketones. Part III.* o-*Hydroxychlorodistyryl Ketones.*

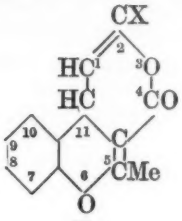
By ISIDOR MORRIS HEILBRON and ROWLAND HILL.

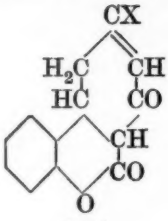
EXPERIMENTS carried out by one of us (J., 1924, **125**, 2064; 1925, **127**, 2159) showed that ethyl acetoacetate reacted with *o*-hydroxydistyryl ketones to give *cyclo*hexenones and that the position taken up by the entering group could be determined by the fact that, when the β-ketonic ester attached itself to the styryl residue adjacent to the *o*-hydroxyl, the carbethoxy-group was eliminated, possibly owing to intermediate coumarin formation. The interactions of ethyl acetoacetate with *2′-chloro-2-hydroxydistyryl ketone* and with the 3′- and *4′-chloro-isomerides* have now been investigated, and the results show that the previous deductions are by no means general. In each case, two products were isolated, a *cyclo*hexenone of molecular formula $C_{23}H_{21}O_4Cl$, and a very small quantity of a second substance of empirical formula $C_{21}H_{15}O_3Cl$, the yield of which decreases progressively as the chlorine atom passes from the ortho- to the para-position. Oxidation of the former by means of potassium permanganate in acetone solution gave the corresponding *o*-, *m*-, or *p*-chlorobenzoic acid, proving that, despite the presence of the carbethoxy-group, addition had taken place at the ethenoid linking adjacent to the *o*-hydroxy-group and consequently the *cyclo*hexenones must be formulated as (I).

The isomeric substances $C_{21}H_{15}O_3Cl$ may be represented either as *2-chlorostyryl-5-methyl-3 : 4-coumalo-6-benzopyrans* (II), or as chlorostyryldihydrocoumarino*cyclo*hexenones (III), resulting through the elimination of a molecule of alcohol from the corresponding *cyclo*hexenones (I). If the latter formulation be correct, it is reasonable to expect that the conversion of the *cyclo*hexenones

into (III) should be possible, but this we have failed to bring about under any of the conditions usually employed for effecting such


(I.)


(II.)


(III.)

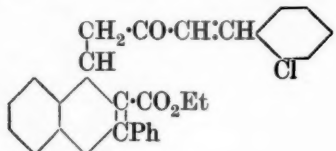
(X = *o*-, *m*-, or *p*-$C_6H_4Cl\cdot CH{:}CH$.)

ring closures. Conversely, attempts to open the supposed dihydrocoumarin ring with formation of the free *cyclo*hexenones have been equally unsuccessful. It would thus seem that these substances cannot be dihydrocoumarino*cyclo*hexenones, and this view is supported by the fact that they fail to give the blood-red coloration with concentrated sulphuric acid characteristic of *cyclo*hexenones of this type (Borsche, *Annalen*, 1910, **375**, 145). They must consequently be formulated in accordance with (II), a type of ring formation reminiscent of that observed by Vorländer (*Annalen*, 1906, **345**, 155) and more recently by Kon and Nutland (J., 1926, 3101), who found that pulegone and *iso*pulegone reacted abnormally with ethyl sodiocyanoacetate, yielding, in place of the expected cyano-esters, the unsaturated cyano-lactones. In order more fully to test this point, 2′-chloro-2-hydroxydistyryl ketone was condensed with benzoylacetic ester. In this case, *cyclo*hexenone formation is precluded, and consequently, if our contentions are correct, a benzopyran and not a dihydrocoumarin derivative should be formed. The product actually isolated proved to be *ethyl* 4-o-*chlorostyracyl*-2-*phenyl*-1 : 4-*benzopyran*-3-*carboxylate* (IV), no trace of a dihydrocoumarin being obtained. The non-isolation of the corresponding coumalobenzopyran may possibly have been due to experimental difficulties, since the semi-solid fraction first deposited resisted all attempts at purification.

In the case of the *o*-hydroxymonostyryl ketones, the β-ketonic ester must of necessity condense adjacent to the hydroxyl group. Forster and Heilbron have already shown (J., 1924, **125**, 340) that the condensation of 2-hydroxystyryl methyl ketone with ethyl acetoacetate leads to 4-acetonyl-2-methyl-1 : 4-benzopyran (V), and a similar type of reaction occurs between 2-hydroxystyryl phenyl ketone and benzoylacetic ester. With 2-hydroxystyryl phenyl ketone, however, these authors state that the reaction leads, in very poor yield, to 3-acetyl-4-phenacyldihydrocoumarin (VI) together

with a solid, m. p. 214°, to which no definite structure was assigned. This reaction has again been investigated under various conditions, but no trace of (VI) has been obtained, 4-*phenacyl*-2-*methyl*-1 : 4-*benzopyran* (VII) being isolated in good yield together with a minute quantity of the substance melting at 214°.

(IV.)



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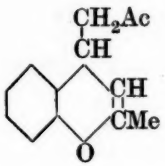
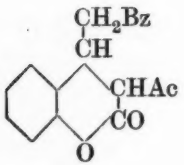
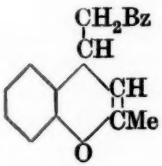
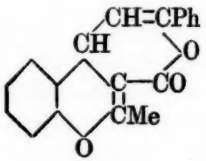




(VI.)



(VII.)



(VIII.)

The constitution of the pyran has been definitely settled by the fact that the condensation of acetylacetone and 2-hydroxystyryl phenyl ketone yields the same product, for which the pyran formula alone is possible. Analysis of the substance, m. p. 214°, indicates that its structure corresponds to 2-*phenyl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran* (VIII), a result in complete harmony with the preceding observations.

An interesting point emerging from this investigation is the fact that, independent of the position of the chlorine atom, the ethyl acetoacetate enters the molecule of the chlorohydroxy-ketone adjacent to the hydroxyl, thus showing that the polar influence of this group completely overweighs that of the halogen substituent, independent of its position in the other styryl residue. The same holds for the *o*-methoxy-ketone, for from 4′-chloro-2-methoxydistyryl ketone ethyl 3-*o*-methoxyphenyl-5-*p*-chlorostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate was formed, identical with the methyl ether prepared by direct methylation of the *cyclo*hexenone obtained from 4′-chloro-2-hydroxydistyryl ketone.

Experimental.

2′-*Chloro*-2-*hydroxydistyryl Ketone*.—2-Hydroxystyryl methyl ketone (30 g.) and *o*-chlorobenzaldehyde (30 g.) dissolved in aqueous sodium hydroxide (120 c.c. of 10%), heat being developed and a clear red solution produced. This was cooled, and a further 120 c.c. of alkali slowly added with constant stirring. After 15 hours, the

sodium salt of the distyryl ketone, which had separated in red, iridescent crystals, was dissolved in warm water, and the ketone liberated as a flocculent, yellow precipitate by carbon dioxide. *2'-Chloro-2-hydroxydistyryl ketone* crystallised from benzene after treatment with blood charcoal in light yellow needles, m. p. 153° (decomp. to a dark green liquid) (yield, 33 g.). It dissolved in aqueous alkali and in concentrated sulphuric acid to blood-red solutions. In place of the yellow form, the ketone was sometimes obtained as bright green plates (Found: C, 71·6; H, 4·6. $C_{17}H_{13}O_2Cl$ requires C, 71·7; H, 4·6%).

2-o-Chlorostyryl-5-methyl-3 : 4-coumalo-6-benzopyran (II).—A mixture of 2'-chloro-2-hydroxydistyryl ketone (20 g.), absolute alcohol (500 c.c.), ethyl acetoacetate (18 c.c.), and aqueous sodium hydroxide (40 c.c. of 20%) was left for 4 days at room temperature, and the orange-red deposit was then collected and repeatedly washed with dilute warm hydrochloric acid and with water. The dried product was crystallised from ethyl acetoacetate and again from much absolute alcohol, from which it separated in long, slender, orange-yellow needles, m. p. 183° (yield, 3·5 g.), sparingly soluble in the usual organic solvents. It dissolved slowly to an orange solution on being warmed with aqueous or alcoholic sodium hydroxide, and in concentrated sulphuric acid it gave an orange-red coloration (Found: C, 71·6, 71·8; H, 4·2, 4·4; Cl, 9·9, 9·9. $C_{21}H_{15}O_3Cl$ requires C, 71·9; H, 4·3; Cl, 10·1%). On boiling under reflux with alcoholic sodium ethoxide, the substance gradually dissolved; acidification then precipitated a solid, which was separated by means of ethyl acetate into two compounds, m. p. 121—122° and 211°, neither of which gave the analytical values required for a *cyclo*hexenone or a pyran derivative. The quantities of these solids were too small to allow of more detailed investigation.

Ethyl 3-o-hydroxyphenyl-5-o-chlorostyryl-Δ^5-cyclohexen-1-one-2-carboxylate (I) was obtained, as a yellow, gummy mass which slowly hardened, by acidifying the filtrate of the above reaction mixture with dilute hydrochloric acid. After being washed, dried, and repeatedly crystallised from benzene in presence of animal charcoal, it was obtained in minute, yellow needles, m. p. 177—178° (yield, 7·5 g.). It was moderately easily soluble in the usual organic solvents and readily soluble in aqueous alkali and gave an intense red coloration with concentrated sulphuric acid (Found: C, 69·3; H, 5·4. $C_{23}H_{21}O_4Cl$ requires C, 69·6; H, 5·3%). Attempts to convert this *cyclo*hexenone into the corresponding dihydrocoumarino*cyclo*hexenone (III) by treatment with aqueous or alcoholic sodium hydroxide, by the use of sodium in xylene and by other means were unsuccessful.

Oxidation.—The hydroxy-*cyclo*hexenone (I) (1 g.), dissolved in acetone (75 c.c.), was treated with potassium permanganate in small quantities; *o*-chlorobenzoic acid, m. p. 134—135°, was isolated from the reaction mixture.

3-o-*Hydroxyphenyl*-5-o-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one.*—The ester (I) (1 g.) was dissolved in glacial acetic acid (20 c.c.) and boiled for 2 hours with sulphuric acid (10 c.c. of 20%). The resultant deep red liquid was poured on a mixture of ice and water, and the precipitated *cyclo*hexenone repeatedly crystallised from ethyl acetate, from which it separated in clusters of yellow plates, m. p. 209—210° (Found: C, 73·8; H, 5·4. $C_{20}H_{17}O_2Cl$ requires C, 74·0; H, 5·2%).

3′-*Chloro*-2-*hydroxydistyryl Ketone.*—The preparation was similar to that of the isomeric 2′-chloro-compound. The sodium salt separated completely, after 15 hours, in black plates with a brilliant green reflex. The *ketone* crystallised from benzene in golden-yellow plates (yield, 72%), m. p. 142—143° (decomp. to a dark green liquid) (Found: C, 71·6; H, 4·6%). This compound also exists in a green modification.

2-m-*Chlorostyryl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran*, after preliminary purification from ethyl acetoacetate, crystallised from absolute alcohol in aggregates of orange-red needles, m. p. 170°, which are sparingly soluble in the ordinary organic solvents (yield, 8%) (Found: C, 71·5; H, 4·4%).

Ethyl 3-o-*hydroxyphenyl*-5-m-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* was obtained from the filtrate and separated from benzene in small, yellow cubes (yield, 30%), m. p. 169° (Found: C, 69·5; H, 5·5%). Oxidation with potassium permanganate in cold acetone solution yielded *m*-chlorobenzoic acid, m. p. 148—149°. 3-o-*Hydroxyphenyl*-5-m-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one* crystallised from ethyl acetate in bright yellow rhombs, m. p. 221° (Found: C, 73·7; H, 5·5%).

4′-*Chloro*-2-*hydroxydistyryl ketone* crystallised from benzene, after treatment with charcoal, in pale yellow plates (yield, 67%), m. p. 152° (decomp. to a dark green liquid) (Found: C, 71·8; H, 4·8%).

2-p-*Chlorostyryl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran* crystallised with difficulty from ethyl acetoacetate in clusters of cream-coloured needles (yield, 1%), m. p. 261—262° (Found: C, 72·1; H, 4·1%). It dissolves in concentrated sulphuric acid to an orange-red solution and is very sparingly soluble in the usual organic solvents.

From the filtrate from which the above compound was separated, *ethyl* 3-o-*hydroxyphenyl*-5-p-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* was obtained as a brown gum on rendering the solution acid. It was repeatedly crystallised from benzene and from ethyl

acetate–light petroleum and was thus obtained in large, golden-yellow plates (yield, 33%), m. p. 199—200° (Found: C, 69·7; H, 5·5%). On oxidation with potassium permanganate in acetone solution it gave *p*-chlorobenzoic acid, m. p. 237°. Methylation with methyl sulphate in acetone solution yielded the methyl ether (m. p. 160°) identical with that obtained by the direct condensation of 4′-chloro-2-methoxydistyryl ketone with ethyl acetoacetate.

3-o-*Hydroxyphenyl*-5-p-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one* was readily obtained by hydrolysing the above ester with 20% sulphuric acid in acetic acid solution. It separated from ethyl acetate in yellow prisms, m. p. 176° (Found: C, 74·3; H, 5·2%).

4′-*Chloro*-2-*methoxydistyryl Ketone*.—The dry sodium salt of 4′-chloro-2-hydroxydistyryl ketone, prepared by condensation as already described, was dissolved in acetone and heated with a slight excess of methyl iodide under reflux for 1 hour. After removal of sodium iodide, the reaction mixture was diluted with water; the yellow oil that separated solidified on being scratched and then crystallised from aqueous acetone in slender, yellow needles, m. p. 74—75° (yield from sodium salt, 92%) (Found: C, 72·5; H, 5·2. $C_{18}H_{15}O_2Cl$ requires C, 72·4; H, 5·0%).

Ethyl 3-o-*Methoxyphenyl*-5-p-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*.—The above ketone (5 g.) was dissolved in absolute alcohol (40 c.c.) and refluxed for 3 hours on a water-bath with ethyl acetoacetate (3 g.) and alcoholic sodium ethoxide (1·6 g.). The hot solution, which was filtered from a small quantity of sodium carbonate, deposited, on cooling, an orange-yellow solid; this was crystallised from methyl alcohol, the cyclo*hexenone* (4 g.) being obtained in small, yellow, rhombohedral plates, m. p. 160° (Found: C, 69·8; H, 5·7. $C_{24}H_{23}O_4Cl$ requires C, 70·2; H, 5·6%). The solution in concentrated sulphuric acid is carmine-red.

Ethyl 4-o-*Chlorostyracyl*-2-*phenyl*-1 : 4-*benzopyran*-3-*carboxylate* (IV).—A hot solution containing 2′-chloro-2-hydroxydistyryl ketone (10 g.), ethyl benzoylacetate (9 g.), and alcohol (50 c.c.) was treated with sodium ethoxide solution (1·7 g. of Na), and the whole left at room temperature for 60 hours. The reaction mixture was then diluted with water and separated from a small quantity of a dark-coloured oil, which gradually solidified but resisted subsequent efforts at purification. The filtrate was diluted to 2000 c.c. and mechanically stirred for several days. On addition of sodium chloride (100 g.), a yellow solid was precipitated which, when crystallised repeatedly from absolute alcohol, separated in colourless needles, m. p. 144—145°. These contain half a mol. of alcohol of crystallisation, which is removed on heating for 5 hours at 110°; the anhydrous compound melts at 195°. The substance slowly

dissolves on warming with aqueous sodium hydroxide and gives a yellow solution with concentrated sulphuric acid (Found : C, 73·0; H, 5·2. $C_{28}H_{23}O_4Cl$ requires C, 73·3; H, 5·0%).

2-*Phenyl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran* (VIII).—A mixture of 2-hydroxystyryl phenyl ketone (11 g.), ethyl acetoacetate (6·5 c.c.), and alcohol (100 c.c.) was treated with alcoholic sodium ethoxide (2·5 g. of Na), and the red solution kept for 18 hours at room temperature. The small quantity of brown solid which separated on dilution with water was repeatedly crystallised from benzene in presence of blood charcoal. The pure substance was thus obtained, in very small yield, in colourless needles, m. p. 214° (Found : C, 78·9; H, 4·6. Calc. for $C_{19}H_{14}O_3$: C, 78·6; H, 4·8%). These figures agree well with those given by Forster and Heilbron (*loc. cit.*, p. 345).

4-*Phenacyl*-2-*methyl*-1 : 4-*benzopyran* (VII) was precipitated from the filtrate of the above reaction mixture on addition of dilute hydrochloric acid. The brown, gummy mass was allowed to harden and repeatedly crystallised from absolute alcohol in the presence of blood charcoal. The *pyran* forms colourless plates, m. p. 171°, which are moderately easily soluble in alcohol, insoluble in cold aqueous alkali, but readily soluble in the hot solution (Found: C, 81·5; H, 6·0. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

Condensation of Acetylacetone with 2-*Hydroxystyryl Phenyl Ketone.*—A boiling solution of 2-hydroxystyryl phenyl ketone (7·5 g.) in alcohol (30 c.c.) and aqueous sodium hydroxide (7·5 c.c. of 40%) was treated with acetylacetone (6 g.) and refluxed for 30 minutes; a further quantity of acetylacetone (6 g.) was then added. After 1 hour, a small quantity of inorganic matter was removed, and the clear solution, on cooling, deposited a mass of yellow needles; a further quantity was obtained by diluting the filtrate. The combined fractions crystallised from alcohol in large, colourless plates, m. p. 169—170°. A mixed melting point with 4-phenacyl-2-methyl-1 : 4-benzopyran, prepared as described above, showed no depression.

We desire to express our thanks to the United Alkali Co., Ltd., for a grant to one of us (R. H.) which enabled this research to be carried out.

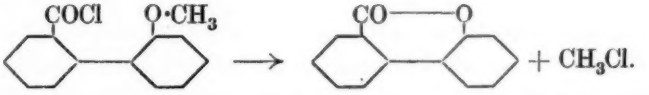
THE UNIVERSITY, LIVERPOOL. [*Received, March 9th*, 1927.]

CXXXIII.—1-*Methoxydiphenyl*-1′-*carboxylic Acid and its Demethylation with Thionyl Chloride.*

By HAROLD GORDON RULE and EGON BRETSCHER.

1-METHOXYDIPHENYL-1′-CARBOXYLIC acid is readily obtained by methylating the lactone of 1-hydroxydiphenyl-1′-carboxylic acid, but the latter substance is unfortunately only available in poor yield (Richter, *J. pr. Chem.*, 1883, **28**, 284; Graebe, *Annalen*, 1895, **284**, 316; Borsche, *Annalen*, 1900, **312**, 225). The reaction between *o*-iodophenyl *o*-iodobenzoate and copper powder at 250° gave very little of the lactone, and under the same conditions, the corresponding bromo-compound failed to react at all. A modification of Borsche's method in which the diazonium sulphate of phenyl *o*-aminobenzoate was warmed in aqueous solution with copper powder produced the lactone in only 14% yield and therefore offers no advantage over that of Borsche (*loc. cit.*).

An unexpected reaction was encountered in an attempt to esterify 1-methoxydiphenyl-1′-carboxylic acid by way of the acid chloride —warming for a few minutes with thionyl chloride demethylated the methoxy-acid quantitatively to the lactone of the hydroxy-acid :



A similar, although less complete, change occurred when the acid was kept for 2 or 3 days with excess of thionyl chloride at room temperature, and when the dried sodium salt was allowed to react at a low temperature with thionyl chloride.

The ease with which this reaction proceeds is remarkable and is presumably due to the close proximity of the –COCl and –OMe groups. Numerous examples of demethylation are recorded in the literature, but these commonly require for their completion several hours' heating at temperatures ranging from 120° to 200°.

EXPERIMENTAL.

Preparation of the Lactone of 1-*Hydroxydiphenyl*-1′-*carboxylic Acid from Phenol and Anthranilic Acid.*—The lactone was prepared according to the directions of Borsche (*loc. cit.*), but the purification was more effective when the dark red product was dissolved in ether and washed several times with ammonia, which also completely removed the colouring matter. After being dried with calcium chloride, the ethereal solution gave the lactone,

which, after recrystallisation from light petroleum, melted at 94—95°. The yield from 60 g. of anthranilic acid and 220 g. of phenol varied from 8·0 to 11·3 g.

Preparation of the Lactone from Phenyl o-Aminobenzoate.—Phenyl *o*-aminobenzoate was prepared in 76% yield by reducing phenyl *o*-nitrobenzoate in alcoholic solution with tin and hydrochloric acid. The reduction is complete in 5 minutes; longer treatment results in loss, owing to hydrolysis of the ester.

The diazotisation also is best conducted in alcoholic solution with amyl nitrite. A solution of phenyl *o*-aminobenzoate (10 g.) in absolute alcohol (120 c.c.) containing the necessary amount of concentrated sulphuric acid (5·0 g.) was cooled to 5°, when crystals of the sulphate separated, and amyl nitrite (5·4 g.) was added. After 2 hours the diazonium sulphate was precipitated with ether (240 c.c.), filtered off, and dried (yield, 13·6 g.).

To a solution of the diazonium salt in 100 c.c. of water, 50 g. of copper powder were slowly added, evolution of nitrogen occurring; the temperature was then raised to 40° during 4 hours. When no more diazonium compound could be detected, the mixture of solids was filtered off, dried, and extracted with chloroform. The solvent was then removed from the extract, the residue hydrolysed with alcoholic potash, and the alkaline liquid acidified. From the mixture of lactone, phenol, and salicylic acid thus obtained, phenol was removed by rapid distillation in steam, which also carried over a little of the lactone, and the liquid was made alkaline with sodium carbonate and extracted with ether. The solution was dried, and on removal of the solvent gave the pure lactone, m. p. 93—94°.

The yield varied with the nature of the copper powder. Ten g. of amino-ester, after diazotisation, gave no lactone at all on treatment with Kahlbaum's "Naturkupfer C." Copper powder which had been prepared according to Gattermann (*Ber.*, 1890, **23**, 1218) and had been dried before use gave 0·8 g. of lactone, whereas the freshly prepared moist powder gave a yield of 1·3 g. (14% of the theoretical).

1-*Methoxydiphenyl*-1′-*carboxylic Acid.*—The solution obtained by heating 10 g. of the lactone with 20 g. of 30% aqueous sodium hydroxide was cooled and shaken for 1 hour with 19 c.c. of methyl sulphate. The methyl ester of the methoxy-acid that separated as an oil was extracted with ether. The aqueous solution deposited on acidification a mixture of the methoxy-acid with a little lactone, from which the pure acid was extracted with sodium carbonate. The *methoxy-acid* crystallised from benzene as a white, crystalline powder, which is very sparingly soluble in water; m. p. 152—153°

(corr.) (yield, 3·5 g.) (Found: C, 73·7; H, 5·5. $C_{14}H_{12}O_3$ requires C, 73·65; H, 5·3%).

The *methyl* 1-*methoxydiphenyl*-1′-*carboxylate* obtained from the above methylation formed a colourless, viscous liquid, b. p. 181—182°/13 mm. (yield, 6·0 g.). It was readily hydrolysed to the methoxy-acid (Found: C, 74·3; H, 6·0. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·8%).

Reaction with Thionyl Chloride.—The thionyl chloride employed was the purified product supplied by the British Drug Houses, Ltd. For confirmatory experiments it was again purified by successive distillations over quinoline and beeswax.

(1) The methoxy-acid (3·10 g.) was heated for a few minutes with an equal weight of thionyl chloride. A considerable quantity of hydrogen chloride was evolved and the excess of thionyl chloride was then removed by warming in a vacuum. The residual crystalline mass, alone or mixed with the pure lactone, melted at 92—93° (yield, 2·63 g. Theoretical yield, 2·69 g.).

(2) The dried, finely powdered sodium salt (12 g.) of the methoxy-acid was added in small portions to 15 g. of thionyl chloride, cooled in ice. On allowing the temperature to rise to that of the room, a slow reaction took place, accompanied by a small evolution of gas. After 3 hours, the thionyl chloride was removed in a vacuum, the residue extracted with benzene at 35°, and the extract treated with menthol and pyridine at 100° for several hours. No menthyl ester could be isolated from the reaction mixture, but 6 g. of crude lactone were recovered, m. p. 85—87°. (A further small quantity was carried over during the steam distillation of the menthol.) A mixture of this with the pure lactone melted at 91—92°.

(3) The methoxy-acid (3·90 g.) was kept for 2—3 days at room temperature with thionyl chloride (10 c.c.), and the unchanged thionyl chloride was then removed in a vacuum, without heating. The residue was a crystalline mass of m. p. 78·5—91·5°, a portion of which, after being warmed for a few minutes in air at 40—45°, melted at 87—91·5° (yield, 3·43 g. Lactone formation requires 3·35 g.). A few decigrams of crude methoxy-acid, together with crude lactone, were recovered by treating part of the product, which still smelt of acid chloride, with water and shaking the mixture with sodium carbonate. Altogether about 2 g. of the pure lactone were recovered. A very small quantity of an unidentified acidic compound containing sulphur was also isolated.

The methoxy-acid was not changed by boiling it for several hours with a saturated aqueous-alcoholic solution of hydrochloric acid, and esterification could be effected in the usual way with dry hydrogen chloride as catalyst.

The authors desire to thank the Earl of Moray Fund for a grant which has covered most of the expense incurred during this investigation.

UNIVERSITY OF EDINBURGH. [*Received, February 17th*, 1927.]

NOTES.

The Mechanism of the Reaction between Aluminium, Iodine, Ethyl Alcohol, and Water. The Preparation of Ethyl Iodide. By A. O. JONES and G. MELLING GREEN.

FURTHER work has thrown much light on the chemistry of the above reaction (J., 1926, 2760). What was thought to be a series of reactions involving the formation of an organo-aluminium complex has shown itself to be one proceeding according to the following scheme:

$$\text{Aluminium} + \text{Iodine} \longrightarrow \text{Aluminium iodide.}$$

$$\text{Aluminium iodide} \underset{\longleftarrow}{\overset{\text{Hydrolysis}}{\longrightarrow}} \text{Hydrogen iodide} + \text{Al(OH)}_3.$$

$$\text{Hydrogen iodide} + \begin{cases} \text{Aluminium} \\ \text{Ethyl alcohol} \end{cases} \longrightarrow \begin{cases} \text{Aluminium iodide} \\ \text{Ethyl iodide} \\ \text{Hydrogen.} \end{cases}$$

Thus the main products of the reaction are ethyl iodide, aluminium iodide, and hydrogen, the hydrogen iodide produced by the hydrolysis of the aluminium iodide distributing itself between the ethyl alcohol and the aluminium in a ratio which depends upon the concentration of the water in the alcohol used.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, January 7th*, 1927.]

New Fluorides of Selenium. By EDMUND BRYDGES RUDHALL PRIDEAUX and CHARLES BERESFORD COX.

Selenium oxyfluoride has been prepared by the action of dry silver fluoride on selenium oxychloride in a platinum bottle, with subsequent distillation and condensation in a platinum condenser (water-cooled). It is a colourless, fuming liquid, with an ozone-like odour similar to that of some organic compounds which have been treated with fluorine. It was analysed after decomposition with water, both by titration with two indicators (J., 1926, 170) and by gravimetric methods. Three separate analyses on quantities of about 1 g. gave the following results, the weights of selenium and fluorine found being referred to the weights of compound taken in calculating

the percentages: Se, 59·1, 59·3, 59·9 (as Ag_2SeO_3); F, 28·3, 28·2, 28·3 (volumetric), 28·3 (as CaF_2). Hence Se (mean), 59·4; F (mean), 28·3 ($SeOF_2$ requires Se, 59·5; F, 28·5%).

Selenium tetrafluoride has been prepared by the same method from silver fluoride and selenium tetrachloride. The first reaction is violent and distillation of the product gives a colourless, fuming liquid having much the same appearance and smell as the oxyfluoride. The first portion of the distillate, collected separately, was deep red, and possibly may contain a lower fluoride, Se_2F_2, formed by the reducing action of the silver present in the silver fluoride. 0·998 G. of this liquid was analysed as described above: Se, 51·8 (as Ag_2SeO_3), 50·6 (as Se); F, 45·5 (volumetric), 46·7 (volumetric HF with gravimetric Se), 46·9 (as CaF_2). Hence Se (mean), 51·2; F (mean), 46·3 (SeF_4 requires Se, 51·0; F, 49·0%).

The properties and reactions of these compounds are being further examined.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, February 26th*, 1927.]

Studies of Precipitated Solids, especially of Strontium and Calcium Sulphates. By PETR P. VON WEIMARN.

THE statement by Bertram Lambert and his collaborators W. Hume-Rothery and J. Schaffer (J., 1926, 2637, 2648) that, previous to their work, no "detailed or systematic study of the effects of the conditions of precipitation upon the type, nature and size of the precipitated particles of strontium sulphate and of calcium sulphate had been carried out" is incorrect. As far back as 1905 I had begun a systematic study of the effects of the conditions of precipitation upon the type, nature, and size of the precipitated particles of different salts. My paper published in 1906 (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 264) included strontium and calcium sulphates amongst the 62 salts investigated, and announced the law that *the mean size of the precipitated crystals decreases with increasing concentration of the reacting solutions*, provided, and this is very important, that the crystallisation process is complete and the course of the process is not disturbed by the influence of variables foreign to the normal reaction. The graphic representation of this law is a curve without a maximum. Curves with maxima are obtained only if the crystallisation process is not complete, if aggregates of crystals are mistaken for individual crystals, or if variables foreign to the normal precipitation process exert an influence.

From the beginning of 1906 my results were published periodically (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 624; *Annals Mining Inst. S. Petersburg*, 1908, **1**, 239; *Jap. J. Chem.*, 1926, **3**, 20; *Koll.-Chem.*

Beih., 1923, **18**, 44, and succeeding years; *Chem. Reviews*, 1925, **2**, 217). Particular mention, with photomicrographs, of the precipitation of strontium and calcium sulphates occurs in my book "Kolloides und Kristalloides Lösen und Niederschlagen," Vol. II, pp. 661—680 and Figs. 90, 91 (Kioto, 1921), and in the second edition of Volume I of this book, "Die Allgemeinheit der Kolloidzustandes," Figs. 92, 93 (Dresden, 1925).

The investigations of Lambert and his collaborators of precipitates of calcium and strontium sulphates are important as independent confirmation of previous work, and are in some respects more detailed. I believe, however, that in other points my investigations (*Koll.-Chem. Beih.*, 1923, **17**, 27) were more extensive, as they included wider limits of concentration and alcoholic as well as aqueous solutions, and colloidal solutions of both salts were obtained.

Subsequently, between 1919 and 1926, detailed investigations of precipitated solids were carried out by Sven Odén (Svedberg, "Formation of Colloids," London, 1921, pp. 94—100, Fig. 20; *Z. Koll.*, 1926, **40**, 92), confirming my results, the latter paper including the examination of strontium sulphate.

As far as I know the literature on the subject, Lambert and his collaborators were the first to study by crystallographic measurement the influence of anions and kations on the precipitation of calcium and strontium sulphates from aqueous solutions and also the influence of certain factors on the transformation of hydrates of strontium sulphate into the anhydrous salt, although I had studied in detail the influence of ions on barium sulphate precipitated from 48% alcohol.—The Imperial Industrial Research Institute, Osaka, Japan. [*Received, March 2nd*, 1927.]

Separation of d-*Neobornylamine from* d-*Bornylamine*. By John Augustus Goodson.

It has been shown by Forster (J., 1898, **73**, 390) that reduction of *d*-camphoroxime with sodium in boiling amyl alcohol yields a mixture of *cis*- and *trans*-isomerides, distinguished as *d*-bornylamine and *d*-neobornylamine, respectively. The isolation of *d*-neobornylamine from this mixture has presented considerable difficulty (compare Forster and Hart-Smith, J., 1900, **77**, 1152; Pope and Read, J., 1910, **97**, 987; 1913, **103**, 454). Separation of the two amines can be effected in the following way.

A mixture of the two amine hydrochlorides (223 g.), resulting from the reduction of *d*-camphoroxime (290 g.), on recrystallisation from water gave a crop of crystals (77·3 g.). An ethereal solution of the bases from the crystals was shaken consecutively with 500

and 300 c.c. of dilute hydrochloric acid (approx. 0·6*N*), giving solutions 1 and 2. A similar solution of the bases from the mother-liquor was shaken with three quantities of 500 c.c. of the dilute acid, giving solutions 3, 4, and 5. These five preparations were evaporated to dryness, giving the following products:

No.	Weight.	$[\alpha]_D$ in dry alcohol ($c = 4·4$).	Bornylamine hydrochloride. Calc.	Neobornylamine hydrochloride. Calc.
1	49·8 g.	+19·1°	46·9 g.	2·9 g.
2	27·5	+12·9	23·6	3·9
3	50·85	+ 3·7	37·15	13·7
4	50·35	− 6·2	29·9	20·45
5	44·5	−22·6	16·6	27·9

Pure *d*-bornylamine hydrochloride was easily obtained from the dextrorotatory fractions by recrystallisation from water as shown by Forster (*loc. cit.*) and Frankland and Barrow (J., 1909, **95**, 2017). The specimen giving the highest rotation had $[\alpha]_D^{20°}$ + 23·3° ($c = 4·4$ in dry alcohol), the previous highest value recorded being + 22·7° (Forster, *loc. cit.*). The ethereal solutions of the bases from the lævorotatory fractions were shaken with small quantities of dilute hydrochloric acid until the $[\alpha]_D$ of the hydrochloride of the base remaining in the ethereal solution became constant. *d*-Neobornylamine hydrochloride having $[\alpha]_D^{20°}$ − 49·4° ($c = 4·4$ in dry alcohol) was thus obtained, the previous highest value recorded being − 44·2° (Forster and Hart-Smith, *loc. cit.*).—WELLCOME CHEMICAL RESEARCH LABORATORIES. [*Received, March 19th*, 1927.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 24TH, 1927, AT 4 P.M.

PROFESSOR H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

The Report of the Council for 1926—1927, together with the Balance Sheets and Statements of Accounts for 1926, was presented, and a statement on the finances of the Society made by the Treasurer. The adoption of the Report was proposed by Mr. E. GRANT HOOPER, seconded by Mr. J. H. COSTE, and carried unanimously.

REPORT OF COUNCIL, 1926–1927.

I. *Fellowship Statistics.*

ON the 31st December, 1925, the number of Fellows was 4083. During the year 1926, 242 Fellows were elected and 16 reinstated, giving a gross total of 4341. The deaths recorded in 1926 were 32, as compared with 40 in 1925, and the resignations 101, as against 88; while the names of 115 Fellows have been removed for non-payment of Annual Subscriptions, the corresponding figure last year being 105. The number of Fellows, therefore, at the 31st December, 1926, was 4093, showing an increase of 10 over the previous year. There are also 23 Honorary Fellows.

During the year the Society has lost one of its distinguished Past-Presidents, Sir William Tilden, who held the office of President from 1903 to 1905, was Treasurer from 1899 to 1903, and served on the Council for a total of 37 years; while by the death of Mr. Josiah W. Kynaston (elected in 1859) the Society has lost its oldest Fellow. The Council has to mourn also the loss of a distinguished Foreign Fellow, Professor Kamerlingh Onnes, who was elected in 1920. A lecture in honour of the memory of Kamerlingh Onnes was delivered by Professor Ernst Cohen, Honorary Fellow, on 10th February, 1927, while an obituary notice of Sir William Tilden will appear in due course in the Journal. The Council would again take the opportunity of recording its appreciation of the services rendered by those Fellows who are good enough to undertake the preparation of the obituary notices for the Journal.

The congratulations of the Society have been conveyed to the following who have attained their jubilee as Fellows:

	Elected.
Henry Chapman Jones	May 4th, 1876.
Harold Holcroft	June 1st, 1876.
Charles Alexander Buckmaster	June 1st, 1876.
Walter Hibbert	June 1st, 1876.

	Elected.
Charles George Matthews	June 15th, 1876.
Channell Law	Nov. 16th, 1876.
Walter Charles Davis	Dec. 7th, 1876.
Arthur Pearson Luff	Feb. 15th, 1877.
Frank Watson Young	Mar. 15th, 1877.

II. *Publications.*

The Journal for 1926 contained 3248 pages, of which 3089 pages were occupied by 437 memoirs and 29 notes, the remaining 159 pages being devoted to Obituary Notices, three lectures, the Report of the General Meeting, and the Presidential Address. The Volume for 1925 contained 409 memoirs and 32 notes, and occupied 2902 pages. During 1926, 528 papers were offered to the Society for publication in the Journal, of which 35 were declined, the corresponding numbers for 1925 being 507 and 37, respectively. The average length of the memoirs for 1926 was 7·0 pages, this being the same as for 1925.

The last Report of Council contained mention of the unsatisfactory arrangements in force for editing the Journal, stating that the matter was receiving attention. After due consideration the Council came to the conclusion that the only way in which adequate editorial assistance could be afforded was to appoint, as a part-time officer, an Assistant Editor, whose duty it should be to relieve the Editor of some of the work and edit the Journal during the absence of the Editor on holiday or through illness. The post was offered to Dr. A. D. Mitchell, who took up his duties in March.

The Council has again to record its indebtedness to those Fellows who undertake the refereeing of papers. Some idea of the magnitude of the work carried out so willingly and efficiently will be obtained if it be borne in mind that each of the 528 papers received during 1926 was submitted to two referees.

III. *Library.*

Excluding the evenings on which meetings of the Chemical Society were held, there were 7692 attendances during the past year, as compared with 6994 in 1925; of these, 5273 were made by Fellows of the Chemical Society and 2419 by members of Contributing Societies, as against 2248 the previous year; while the number of books borrowed during 1926 was 5353, as against 4950 in 1925.

Additions to the Library comprise: 295 books, of which 111 were presented, 593 volumes of periodicals, and 48 pamphlets; the corresponding figures in 1925 being 265, 609, and 163, respectively.

The Library now contains 30,899 volumes, consisting of 9361 books and 21,538 bound volumes of periodicals.

The facilities for "Photostat" copying continue to be increasingly utilised, 2084 pages of printed matter having been copied, as against 1266 pages in 1925.

IV. *General.*

In the last Report of Council, the hope was expressed that the decision to hold the Annual General Meeting and Dinner from time to time elsewhere than in London would commend itself to Fellows resident in the provinces. It is satisfactory to report that the attendance at the Annual General Meeting held in the University of Manchester and at the Dinner at the Midland Hotel was such as to justify the Council in the course taken. The appreciative thanks of the Council have been conveyed to the local Committee, which undertook the arrangements for the meeting and the dinner.

In addition to the Kamerlingh Onnes Memorial Lecture, two lectures have been delivered during the year. An informal lecture was given in the Society's Rooms on April 29th, 1926, by Professor W. E. S. Turner on "The Physical Properties of Glasses; the Relationship of Chemical Composition and Mode of Preparation," and the Hugo Müller Lecture was delivered at the Institution of Mechanical Engineers by Professor S. P. L. Sörensen, of Copenhagen, who took as the title of his lecture "The Composition and Characterisation of Genuine Proteins."

The lectures continue to be well attended by Fellows, and the Council is deeply indebted to those who place their services at the disposal of the Society in this connexion.

Professor Richard Willstätter, of Berlin, has accepted the invitation of the Council to deliver the Faraday Lecture for 1927, entitled "Problems and Methods in Enzyme Research," to be given at the Royal Institution (by kind permission of the Managers) on the 18th May.

The Society was represented by Professor H. E. Armstrong and Sir William Pope at the Congress of Pure and Applied Chemistry and the Cannizzaro Celebrations, organised by the Associazione Italiana di Chimica, held in Palermo in May; an Address of Congratulation was presented. The President attended as the Society's delegate the Congress of Chemists held in London in July; while at the 6eme Congrès de Chimie Industrielle, held in Brussels in September, the Society was represented by Professor C. S. Gibson and Professor J. F. Thorpe. An Address of Congratulation was presented to the University of Sheffield on the occasion of its Coming-of-Age Celebrations, which the President and the Treasurer attended on behalf of the Society, and also to the American Chemical

Society at the Celebrations of its 50th Anniversary held in Philadelphia in September.

Professor C. S. Gibson, Sir William Pope, and Professor J. F. Thorpe were appointed the Society's delegates on the Federal Council for 1927; Dr. T. Slater Price agreed to represent the Society for two years on the Editorial Board of the "Journal of Physical Chemistry," in the place of Professor T. M. Lowry, the Faraday Society being represented by Dr. E. K. Rideal; while Professor C. S. Gibson was nominated to give evidence on behalf of the Society before the Sub-Committee appointed to consider the existing practice relating to the method of preparing the British Pharmacopœia.

The Society's representatives on the Bureau of Chemical Abstracts for the year 1926—1927 are Professor C. S. Gibson, Dr. J. T. Hewitt, Professor G. T. Morgan, and Professor J. F. Thorpe.

The year 1926 has seen the introduction of the larger format for the "A" section of "British Chemical Abstracts," a change which, although perhaps unwelcome at first to some Fellows, represents a definite advance towards the co-ordination of chemical publication in this country. The first Annual Index covering abstracts in both pure and applied chemistry, rendered possible by the unification of format, has been prepared and will be issued in due course. The elimination of the overlap as between the "A" and "B" sections, and other changes of a minor character, such as the reduction of the space between successive abstracts and the condensation of the monthly author index, constitute definite economies in the cost of producing the "A" abstracts.

The hearty thanks of the Council have been conveyed to Mrs. Alec Tweedie, who has presented to the Society a valuable portrait in oils of Liebig by Trautschold, together with some of his original letters. Particular interest is given to the portrait, which hangs on the walls of the staircase, by the fact that it is the only oil painting for which Liebig sat. Valuable additions have been made to the Society's collection of medals by the presentation of those awarded to the late Sir Edward Thorpe, and of the Le Blanc, Mond, and other medals.

The Longstaff Medal for 1927 has been awarded to Professor Robert Robinson for his researches in Organic Chemistry. The Harrison Memorial Prize Selection Committee has made its first award, nominating Dr. Charles R. Harington as the recipient of the Harrison Memorial Prize for 1926 for his work on thyroxine. Presentation of these two awards will be made at the Annual General Meeting.

After consideration of the question of limiting the term of service

by Fellows on the various Committees, the Council decided that as from April next no Fellow other than an Officer shall serve for more than five consecutive years on any Committee.

The Council desires to thank those Fellows and others who have agreed to contribute to the Annual Reports for 1926.

The Council Room has been relighted and re-decorated, and two walls have been lined with adjustable steel bookshelves. The portraits of Past-Presidents which, it was stated in the last report, would be placed in a portfolio, have been re-hung in the Meeting Room, thus rendering it unnecessary, in the opinion of the Council, for the names of the Past-Presidents to be inscribed on oak panels.

The Council received in April a request from Col.-Sergt. G. W. Holland to be allowed to retire in September, by which time he would have completed 24 years' service. The resignation was accepted with much regret, and in recognition of his loyal services the Council has granted a pension of £120 while Col.-Sergt. and Mrs. Holland are both alive; in event of the death of either, the proportion of the pension to be paid to the survivor will be determined by the Council then in office. A suitably inscribed tea-tray and a purse of £66 0*s.* 6*d.*, to which members of Council and other Fellows had been invited to subscribe, were also presented to him.

The applications for Research Grants received during the year amounted to £1337 15*s.*, the sum granted being £772 (see Proceedings 1926, pp. 84 and 128). It has been decided that in future every applicant who is carrying out the research under direction should have the application initialled by his supervisor, and that if a grant be made to anyone whose permanent residence is not in this country, the supervisor, under whom the Grantee is working, shall be asked to receive the Grant and to assume responsibility for the furnishing by the Grantee of a proper report.

Financial.

The balance representing excess of ordinary income over ordinary expenditure is £135, but there is a nominal adverse balance representing excess of extraordinary expenditure over extraordinary income of £421. This is due to the cost of providing new book-cases in the Council Room (£221), which has been carried to Balance Sheet, and to the transfer of £200, part of last year's balance, from the General Purposes Balance Sheet to the Staff Pensions Fund Balance Sheet.

Income. The ordinary income of the Society has increased during the year by £612 4*s.* 3*d.* This new income has chiefly been derived from the following sources: (1) Increase in annual sub-

scriptions, £234; (2) increase from sales of publications, £370 2*s*. 1*d*. and (3) an advance of £139 2*s*. 4*d*. in the income derived from the Publications Fund. There have, however, been decreases in the incomes obtained by the sale of the Journal to the public and from advertisements.

Expenditure. The ordinary expenditure of the Society has increased by £943 8*s*. 6*d*. over that of 1925. The chief cause of this increase is to be found in the cost of the Journal, which is £405 16*s*. 8*d*. greater than last year. The appointment of a part-time Assistant Editor in March accounts for £153 17*s*. of this increase, the remainder, £251 19*s*. 8*d*., being due to the growth of the Journal by 346 pages. Actually, the cost per page of the Journal is 5*d*. less this year than last, being £1 15*s*. 6*d*. for 1926 and £1 15*s*. 11*d*. for 1925. Other causes of the increased expenditure are to be found in an advance in the cost of the Annual Reports of £107 4*s*. 2*d*., due to an increase in the size of the volume which, it is believed, will not recur, and in the expense entailed by the superannuation scheme, namely £176 5*s*. 2*d*. on behalf of the general staff and £88 15*s*. on behalf of the Library staff, which the Society has had to meet for the first time this year. The items under "House Expenses and Repairs" and "Furniture" show an increase of £116 9*s*. 11*d*. This has been caused by the need for providing new floor coverings for the inner library (tea-room), for the office, and for the redecoration and relighting of the Council Room; it has also been necessary to provide the office with additional furniture. Nevertheless, despite this extra expenditure, the general administrative expenses have increased by only £8 0*s*. 9*d*. owing mainly to the exercise of economy in other directions and to the transference of part of the expenses to the Library Account.

The general financial position of the Society could, therefore, be regarded as satisfactory were it not for the fact that it is evident, from the increase in the volume of chemical publications both this year and last, that the curve representing the world's annual output of new chemical knowledge is still rising. A steadily increasing expenditure due to this cause cannot be met by the establishment of any capital fund, because it is clear that such a fund would have to be augmented by some £5000 yearly to be of any service. It can only be met by providing new income in other ways, and, in this connexion, it must be remembered that during the past five years the ordinary annual income of the Society has been increased by £3594, or, in other words, that the income for 1926 is greater by that amount than the income for 1921. This has been accomplished without raising the subscription, and, in consequence, there are now not many new sources of income that

can be made available. A few years will show whether this increase in material which must be published is normal and recurrent, for, if it should prove to be so, the Council will have to consider in what way the situation can be met.

Library Account. In order to present a more complete picture of the annual cost of the Library and of the manner in which the participating Societies contribute towards its maintenance, the account has, this year, been printed as a separate item, in which the superannuation charges of the Library staff and a proper proportion of the general overhead administrative charges are included. For these reasons the item of £2093 11*s.* 6*d.*, for Library Expenses, appearing in the General Income and Expenditure Account as against £1799 2*s.* 3*d.* for last year, does not wholly represent an increase in the cost of the Library, because the difference includes superannuation charges and general expenses (amounting to £215 9*s.* 11*d.*), the latter of which has hitherto been included in the General Account.

Publications Fund. The capital of the Fund now stands at £7170 3*s.* 9*d.* The donations for the year amount to £1102 9*s.*, and the subscriptions to £85 18*s.* The sum of £1500 has been invested during the year, and with this £491 7*s.* 0*d.* Five per cent. War Stock and £1310 5*s.* 5*d.* Three and a half per cent. Conversion Stock have been purchased. In addition, the Society received £1800 Five per cent. War Stock transferred at par from the Pedler estate, so that the sum invested on the Publications Fund Account has been increased by £3300. The Fund has contributed £761 16*s.* 2*d.* towards the cost of the Society's publications, but £350 of this was derived from the Government Publication Grant of the Royal Society, for which the Council desires to express its acknowledgment and thanks. Life composition fees amounting to £190 10*s.* have been transferred to the Capital Account. It is a matter for regret that further delays occurred in distributing the estate of the late Sir Alexander Pedler. However, at a meeting of representatives of the four Societies concerned under the Will, a scheme of distribution was agreed on, the negotiations being placed in the hands of Messrs. W. B. Keen and Co. The final distribution of the estate was made early in 1927, too late to be included in the present accounts, and in future the Publications Fund Account will benefit by the full amount of interest accruing each year from the Pedler Bequest.

Special Publications Fund. In response to a request frequently made for photographs of Chemists, it was decided to publish, as an experiment, portraits of the following eight Chemists: R. W. Bunsen, Emil Fischer, A. W. von Hofmann, D. I. Mendeléeff,

Louis Pasteur, Sir William Perkin, Sir William Ramsay, and Sir Henry E. Roscoe. There is a steady demand for these portraits, which are reproduced by a photolithographic process, and the venture is being financed by the Special Publications Fund Account. The cost of these portraits was £171 14*s*. 10*d*., and already £72 3*s*. 11*d*. has been obtained by their sale. The sale of the Memorial Lectures, Vol. I., has realised £43 2*s*., making, with the amount received last year, a sum of £95 12*s*. towards the original cost of £225 3*s*.

Staff Superannuation Scheme. The decision of the Council, made last year, to establish a staff superannuation scheme on a contributory basis has this year, as mentioned elsewhere, caused an increase in the ordinary expenditure of £176 5*s*. 2*d*. on behalf of the general staff and of £88 15*s*. in respect of the Library. During the year, £159 12*s*. has been contributed by Fellows to the Staff Pensions Fund, and this, together with the sum of £200 transferred during the year from the General Fund, has brought the capital of the Fund to £377 15*s*. 11*d*. The Council wishes to thank those Fellows who have contributed to the Fund, but desires to emphasise the need for further donations in order that the Fund may serve the purpose for which it has been established. The sum of £51 15*s*. has been paid out in pensions during the year.

Sales of Publications. As a result of the increased price charged to the public for the Abstracts in Pure Chemistry for 1926, the income received from this source has been increased by £371 12*s*. 4*d*. There is, however, a decrease in the amount received from the sale of the Journal of £32 3*s*. 1*d*. The sale of the Annual Reports realised £767 1*s*. 11*d*., as against £759 3*s*. 3*d*. last year, and it is evident that in the present circumstances the Council cannot afford to relinquish any part of this important source of income by remitting the charge which Fellows have at present to pay for this publication.

A vote of thanks to the Auditors (Prof. A. J. Allmand, Prof. J. S. S. Brame and Dr. G. W. Monier-Williams), proposed by the TREASURER and seconded by Dr. P. C. AUSTIN, was carried, acknowledgment being made by Dr. G. W. MONIER-WILLIAMS.

It was moved from the Chair and carried unanimously that Drs. O. L. Brady, A. E. Dunstan, and G. W. Monier-Williams be elected Auditors for the coming year.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council and Committees for their services during the past year was proposed by Dr. J. A. VOELCKER, seconded by Prof. A. FINDLAY, and carried unanimously, response being made by Prof. J. C. PHILIP.

In presenting the Longstaff Medal for 1927 to Prof. R. Robinson, the PRESIDENT stated:

"PROFESSOR ROBINSON,

"The award which I am about to make is the highest distinction which the Chemical Society can bestow on one of its Fellows, and the Council believes that the present award will meet with the cordial approval of all the Fellows of the Society.

"Your investigations of the chemistry of the alkaloids have not only elucidated the structure of some of these extremely complicated substances but have also indicated in a striking manner the possible mechanism of the processes by which they may be formed in Nature. You have also achieved outstanding success in your inquiries into the constitution and synthesis of the colouring matters of flowers and in your studies of the mechanism of reactions in Organic Chemistry. All this work has secured for you a place in the foremost rank of Organic Chemists and you have conferred distinction on British Chemistry.

"It is with the very greatest pleasure that I now award you the Longstaff Medal, and, on behalf of the Council and Fellows, express the hope that your work in the future will be crowned with even greater success than it has been in the past."

THE PRESIDENT said that it had been found possible to make the first award of the Harrison Memorial Prize under the terms of the Trust Deed and that the Prize for 1926 had been awarded to Dr. Charles R. Harington. In making the presentation, the PRESIDENT said:

"DR. HARINGTON,

"The Harrison Memorial Prize is given for conspicuously meritorious work in any branch of chemistry pure or applied, and is regarded as an exceptional distinction to commemorate Edward Frank Harrison.

"Your ably conducted investigations have led to a greatly improved method for separating the pure hormone from the thyroid gland and finally to the synthesis of thyroxine indistinguishable chemically and physiologically from the natural thyroxine. This work constitutes such a notable contribution to chemical knowledge that the Selection Committee is justified in awarding you the Prize for 1926 in accordance with the terms of the Trust Deed.

"On behalf of the Harrison Memoria Prize Selection Committee, I award you the Harrison Memorial Prize and express

the hope that your future work will be even more successful than that which you have already accomplished."

THE PRESIDENT then delivered his address entitled :—"Experiments on Molecular Complexity." A vote of thanks to the PRESIDENT for his services in the Chair during the past year, and for his address, with the request that he would allow the Address to be printed in the Journal, was proposed by Prof. W. P. WYNNE, seconded by Prof. A. LAPWORTH, and carried with acclamation, the PRESIDENT making acknowledgment with thanks.

The report on the election to vacancies on the Council for the year 1927—1928 was read as follows :

President.—H. Brereton Baker.

Vice-Presidents who have filled the office of President.—H. E. Armstrong, H. B. Dixon, Percy F. Frankland, Alexander Scott, W. P. Wynne.

Vice-Presidents who have not filled the office of President.—J. B. Cohen, G. G. Henderson, Sir Robert Robertson, R. Robinson, N. V. Sidgwick, Arthur Smithells.

Treasurer.—Jocelyn F. Thorpe.

Secretaries.—T. Slater Price, C. S. Gibson.

Foreign Secretary.—F. G. Donnan.

Ordinary Members of Council.—M. P. Applebey, H. Bassett, E. R. Bolton, H. V. A. Briscoe, J. E. Coates, J. C. Drummond, F. A. Freeth, F. W. Gamble, R. Whytlaw-Gray, J. Kenyon, T. J. Nolan, K. J. P. Orton, R. H. Pickard, B. D. Porritt, E. K. Rideal, J. F. Spencer, G. Stubbs, F. J. Wilson.

INCOME AND EXPENDITURE ACCOUNT

1925 £ s. d.	£ s. d.	*Income.*	1926 £ s. d.	£ s. d.
	123 0 0	To Life Compositions		190 10 0
		,, Annual Subscriptions :—		
1083 0 0		Received in advance, on account of 1926	1054 10 0	
8130 0 0		,, during 1926 ,, ,, ...	8318 10 0	
446 8 0		,, ,, ,, ,, 1925	497 12 0	
16 10 0		,, ,, ,, ,, 1924 and previous years	39 8 0	
9675 18 0			9910 0 0	
500 0 0		*Less* amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	500 0 0	
9175 18 0			9410 0 0	
500 0 0		*Add* Arrears at date: £886 8s.; Estimated to realise as per Balance Sheet	500 0 0	
	9675 18 0			9910 0 0
		,, Investments, Dividends on :—		
24 11 11		£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	25 3 10	
35 18 8		£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock, 1914/54	36 10 0	
35 0 0		£1400 India 2½ per cent. Stock	35 0 0	
48 0 0		£2400 Bristol Corporation 2½ per cent. Debenture Stock	48 0 0	
84 15 7		£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	86 16 4	
28 7 0		£1200 Leeds Corporation 3 per cent. Stock	28 16 0	
45 0 0		£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53 ...	45 0 0	
28 2 6		£1200 London and North Eastern Railway 3 per cent. Debenture Stock	28 16 0	
19 5 10		£700 Canada 3½ per cent. Stock, 1930/50	19 12 0	
105 0 0		£2100 5 per cent. War Stock, 1929/47	105 0 0	
44 0 0		£1100 5 per cent. War Bonds, 1929/47	44 0 0	
24 0 0		£600 Funding Loan, 4 per cent., 1960/90	24 0 0	
374 0 0		£11873 3½ per cent. Conversion Stock	392 9 0	
137 5 3		,, Income Tax Recovered	114 0 0	
51 4 11		,, Interest on Deposit	55 7 10	
	1084 11 8			1028 11
		,, Publication Sales :—		
2663 11 0		Journals and Proceedings	2631 7 11	
2067 0 7		Abstracts	2438 12 11	
64 4 6		Collective Index, Vols. I–VI	113 10 4	
759 3 3		Annual Reports on Progress of Chemistry	767 1 11	
22 0 0		Berichte	—	
—		Memorial Lectures. Vol. II.	27 9 0	
—		Other Publications	9 4	
5575 19 4			5978 11 5	
513 19 9		*Less* Publishers' Commission	546 9 9	
	5061 19 7			5432 1 8
596 17 0		,, Proceeds of Advertisements in Journal and Abstracts ...	538 1 5	
57 11 8		*Less* Commission	148 1 9	
	539 5 4			389 19 8
	25 10 9	,, Miscellaneous Receipts...		30 2 11
	681 15 0	,, Donations to Library		682 16 0
	28 17 6	,, Subscriptions from other Societies		29 18 6
		,, Transfer from Publications Fund, viz. :—		
350 0 0		Government Publications Grant (through the Royal Society)	350 0 0	
184 3 4		Dividends and Interest on Deposit	325 18 2	
88 10 6		Subscriptions	85 18 0	
	622 13 10			761 16
	£17,843 11 8			£18,455 15
	80 0 0	To Pedler Bequest, Income from Residue of Estate of Sir Alexander Pedler		143 19
	—	,, Pedler Bequest, on Account of Capital		1800 0 0
	—	,, Excess of extraordinary Expenditure over extraordinary Income, carried to Balance Sheet		421 0 0
	£80 0 0			£2,364 19 4

FOR THE YEAR ENDED 31ST DECEMBER, 1926.

1925 £ s. d.	1925 £ s. d.	*Expenditure.*	1926 £ s. d.	1926 £ s. d.
		By Expenses on account of Journal :—		
869 0 0		Editorial Salaries	995 7 0	
69 10 7		Editorial Postages	68 5 1	
3423 15 1		Printing of Journal	3673 7 1	
69 7 5		Binding	88 11 4	
128 17 8		Printing of Advertisements	73 12 7	
5 14 1		Addressograph Labels	5 9 9	
474 9 5		Distribution of Journal	510 7 11	
312 8 9		Authors' Copies	336 14 8	
5 5 0		Insurance of Stock	5 5 0	
5 10 2		Warehousing of Stock	17 11	
—		Miscellaneous	11 16 11	
	5363 18 2			5769 14 10
		,, Expenses on account of Abstracts :—		
1035 0 0		Editorial Salaries	1150 15 0	
34 10 0		Editorial Postages	39 16 11	
1237 11 11		Abstractors' Fees	1194 11 6	
3026 8 10		Printing of Abstracts	3073 5 3	
69 7 4		Binding	88 11 4	
5 14 2		Addressograph Labels	5 9 8	
474 9 5		Distribution of Abstracts	510 8 0	
5 5 0		Insurance of Stock	5 5 0	
5 10 2		Warehousing of Stock	17 10	
61 17 2		Miscellaneous	55 15 11	
	6055 14 0			6124 16 5
	27 11 6	,, Lecture Expenses		36 14 8
	84 17 3	,, Advance Proofs and Reports of Meetings		90 12 7
	528 15 1	,, Annual Reports on the Progress of Chemistry		635 19 3
	13 18 10	,, Purchase of Back Numbers of Publications		40 8 10
	126 2 0	,, List of Fellows—Printing, etc.		—
	1799 2 3	,, Library Expenses		2093 11 6
		,, Donations :—		
100 0 0		Annual Tables of Constants	—	
50 0 0		British Empire Exhibition	—	
—		Optical Conventions	10 10 0	
—		Federal Council	100 0 0	
	150 0 0			110 10 0
		,, Administration Expenses :—		
1427 12 9		Salaries of Staff	1436 13 6	
414 6 0		Wages (Commissionaire, Housekeeper, and Charwomen	412 14 6	
16 5 0		Pensions	—	
83 12 1		Coal and Lighting	57 4 1	
109 16 3		House Expenses and Repairs	153 2 10	
—		Furniture	73 3 4	
22 0 2		Telephone	22 16 0	
43 0 3		Tea Expenses	34 4 7	
25 0 4		Insurances	24 16 4	
31 10 0		Accountants' Charges	31 10 0	
6 17 3		Commission on Recovery of Income Tax	5 14 0	
472 3 7		Miscellaneous Printing and Stationery	446 16 0	
201 13 1		Postages	155 6 8	
10 10 0		Legal Charges	—	
—		Expenses at Annual General Meeting at Manchester	35 0 7	
16 7 11		Carriage on Journals to Germany	—	
16 0 0		New Press and Renovating Seal	—	
14 14 0		Addresses	19 2 0	
80 8 3		Miscellaneous Expenses	91 13 3	
	2991 16 11			2999 17 8
	—	,, Superannuation of Staff		*176 5 2
	123 0 0	,, Transfer to Publications Fund (Life Composition Fees)		190 10 0
	112 11 5	,, Collective Index Vol. VI		—
	—	,, Staff Pensions Fund—Pensions paid during 1926		51 15 0
		,, Excess of ordinary Income over ordinary Expenditure carried to Balance Sheet		135 0 0
	£17,843 11 8			£18,455 15 11
	80 0 0	By Publications Fund—Income from Pedler Bequest		143 19 4
	—	,, Publications Fund—Capital from Pedler Bequest		1800 0 0
		,, Staff Pensions Fund, transferred from accumulation of General Purposes Account at 31st December, 1925		200 0
	—	,, Cost of New Library Bookshelves		221 0
	£80 0 0			£2,364 19 4

* A further £88 15s. 0d. is included in Library Expenses.

Income and Expenditure Accounts of other Funds for the Year ended 31st December, 1926.

RESEARCH FUND.

1925	*Income.*	1926		1925	*Expenditure.*	1926	
£ s. d.		£ s. d.	£ s. d.	£ s. d.		£ s. d.	£ s. d.
	To Dividends on:			758 10 0	By Grants		772 0 0
31 5 0	£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock ...	32 0 0		2 10 10	,, Commission on Recovery of Income Tax...		1 7 0
20 3 11	£1034 Great Western Railway 2½ per cent. Stock	20 13 8		5 18 0	,, Advertisements, etc.		6 19 0
34 5 8	£1142 16s. New South Wales 3 per cent. Stock	34 5 8		—	,, Honorarium to Lecturer		21 0 0
33 13 2	£1122 Metropolitan Water Board 3 per cent. "B" Stock	33 13 2		—	,, Balance, being Excess of Income over Expenditure, carried to Balance Sheet ...		27 3 9
26 13 1	£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	27 5 10					
19 0 10	£806 Victoria 3 per cent. Stock, 1929/49	19 6 10					
224 18 6	£4498 11s. 0d. 5% War Loan, 1929/47 ...	224 18 6					
192 7 0	£5164 13s. 9d. 3½% Conversion Stock ...	180 15 2					
			572 18 10				
50 17 4	,, Income Tax Recovered		27 0 0				
111 5 8	,, Repayment of Grants		180 15 0				
4 17 0	,, Interest on Deposit		15 19 6				
—	,, Sale of Apparatus		31 16 5				
17 11 8	,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		—				
£766 18 10			£828 9 9	£766 18 10			£828 9 9

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

	To Dividends on:—			2 4 6	By Advertisements		5 4 6
25 0 0	£500 National War Bonds, 5%, 1928 ...	25 0 0		—	,, Cost of Plaque..		135 0 0
25 0 0	£500 National War Bonds 5%, 1929 ...	25 0 0		54 8 3	,, Balance, being excess of Income over Expenditure, carried to Balance Sheet		—
2 3 2	£61 15s. 8d. Conversion Stock, 3½% ...	2 3 2					
4 9 7	Interest on Deposit	3 9 2					
			55 12 4				
—	,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		84 12 2				
£56 12 9			£140 4 6	£56 12 9			£140 4 6

PUBLICATIONS FUND.

1925	*Income.*	1926		1925	*Expenditure.*	1926	
£ s. d.		£ s. d.	£ s. d.	£ s. d.		£ s. d.	£ s. d.
	To Dividends on:			1,000 0 0	By Grants		1,000 0 0
31 5 0	£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock ...	32 0 0		2 10 10	,, Commission on Recovery of Income Tax...		1 7 0
20 3 11	£1034 Great Western Railway 2½ per cent. Stock	20 13 8		5 18 0	,, Advertisements, etc.		6 19 0
34 5 8	£1142 16s. New South Wales 3 per cent. Stock	34 5 8		—	,, Honorarium to Lecturer		21 0 0
33 13 2	£1122 Metropolitan Water Board 3 per cent. "B" Stock	33 13 2		—	,, Balance, being Excess of Income over Expenditure, carried to Balance Sheet ...		27 3 9
26 13 1	£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	27 5 10					
19 0 10	£806 Victoria 3 per cent. Stock, 1929/49	19 6 10					
224 18 6	£4498 11s. 0d. 5% War Loan, 1929/47 ...	224 18 6					
192 7 0	£5164 13s. 9d. 3½% Conversion Stock ...	180 15 2					
			572 18 10				
50 17 4	,, Income Tax Recovered		27 0 0				
111 5 8	,, Repayment of Grants		180 15 0				
4 17 0	,, Interest on Deposit		15 19 6				
—	,, Sale of Apparatus		31 16 5				
17 11 8	,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		—				
£766 18 10			£828 9 9	£766 18 10			£828 9 9

PUBLICATIONS FUND.

1925	*Income.*	1926		1925	*Expenditure.*	1926	
£ s. d.		£ s. d.		£ s. d.		£ s. d.	£ s. d.
	To Transfer from General Account, being Life				By Transfer to General Account—Income applicable to 1926 Publications, viz.:—		
123 0 0	Composition Fees for year...	190 10 0			,, Government Publications Grant (through		
101 0 6	,, Subscriptions	99 0 0		350 0 0	the Royal Society)	350 0 0	
2395 14 4	,, Donations	1102 9 0		184 3 4	,, Dividends and Interest on Deposit	325 18 2	
20 19 2	,, Interest on Deposit	4 19 0		88 10 6	,, Subscriptions	85 18 0	
	,, Government Publications Grant (through						761 16 2
350 0 0	the Royal Society)	350 0 0		—	,, Commission on recovery of Income Tax ...		9 3
	,, Dividend on £5,933 10*s.* 2*d.* Conversion			12 10 0	,, Subscriptions in advance		13 2 0
83 4 2	Stock, 3½ per cent.	152 8 6			,, Balance, being excess of ord. Income over		
—	,, Dividend on £491 17*s.* War Stock, 5%, 1929/47	24 11 4		2438 14 4	ord. Expenditure, carried to Balance Sheet		1157 15 1
—	,, Income Tax recovered	9 4 8					
£3073 18 2		£1933 2 6		£3073 18 2			£1933 2 6
	To Transfer from General Purposes Account.				By Balance, being excess of extraordinary		
80 0 0	Income from Pedler Bequest	143 19 4			Income over extraordinary Expenditure		
—	,, Ditto on account of Capital	1800 0 0		80 0 0	carried to Balance Sheet		1943 19 4
£80 0 0		£1943 19 4		£80 0 0			£1943 19 4

SPECIAL PUBLICATIONS FUND.

	To Sales :—				By Cost of Reproduction :—		
52 10 0	Memorial Lectures, Vol. I	43 2 0.		225 3 0	Memorial Lectures, Vol. I		—
—	Portraits	72 3 11		—	Printing Portraits of Eminent Chemists		171 14 10
		115 5 11		—	,, Advertising		17 6 6
	Less Commission	4 16 11		—	,, Miscellaneous Expenses		1 2
			110 9 0				
—	,, Dividend on £2115 8*s.* 10*d.* Conv. Stock, 3½%		59 4 8				
—	,, Interest on Deposit...		9				
	,, Balance, being Excess of Expenditure over						
172 13 0	Income carried to Balance Sheet		19 8 1				
£225 3 0			£189 2 6	£225 3 0			£189 2 6

STAFF PENSIONS FUND.

15 15 0	To Subscriptions	—		—	By Pensions paid during 1926		51 15 0
	,, Transfer from General Account (from				,, Excess of Income over Expenditure carried		
—	accumulation of Funds)	200 0 0		15 15	to Balance Sheet		362 0 11
	,, Ditto from General Account (to meet						
—	pensions for current year)	51 15 0					
—	,, Donations...	159 12 0					
—	,, Interest on Deposit...	2 8 11					
£15 15 0		£413 15 11		£15 15 0			£413 15 11

LIBRARY.

1925	*Income.*	1926	1925	*Expenditure.*	1926
£ s. d.		£ s. d. £ s. d.	£ s. d.		£ s. d. £ s. d.
	To Donations:—		1185 10 0	By Salaries	1222 17 6
	Association of British Chemical Manu-		—	,, Superannuation of Staff	88 15 0
250 0 0	facturers	250 0 0	483 7 6	,, Books and Periodicals	526 11 4
10 10 0	Biochemical Society	10 10 0	130 4 9	,, Binding	128 12 9
5 5 0	Faraday Society	5 5 0		,, Printing, Stationery and Postage	42 2 4
45 0 0	Institute of Brewing	45 0 0		,, Lighting, Heating, Furniture, etc.	79 7 4
250 0 0	Institute of Chemistry	250 0 0		,, Miscellaneous	5 5 3
100 0 0	Society of Chemical Industry	100 0 0			
10 0 0	Society of Dyers and Colourists	10 10 0			
10 10 0	Society of Public Analysts	10 10 0			
—	Jones, J. P.	1 1 0			
—	,, Contribution from General Fund	1410 15 6			
		£2093 11 6			£2093 11 6

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31ST DECEMBER, 1926.

GENERAL PURPOSES.

Liabilities.			*Assets.*		
£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
To Subs. received in advance:—			By Investments (value when acquired):—		
1060 10 0 at £3 0 0 ...		942 0 0	£737 London, Midland and Scottish		
,, Sundry Creditors (Printing and other			839 3 7 Railway 4 cent. Debenture Stock ...	839 3 7	
2905 2 6 Expenses)		2221 10 7	1650 0 0 £1520 14s. 3d. Cardiff Corpn. 5% Stock	1650 0 0	
— ,, Bankers—overdraft		464 9 8	1316 1 0 £1400 India 2½ per cent Stock	1316 1 0	
,, Excess of Assets over Liabilities as			£2400 Bristol Corpn. 2½% Debenture		
25,660 6 5 per last Balance Sheet	26,126 10 8		2070 2 0 Stock, Bristol Dock Account	2070 2 0	
Add Excess of Income over Ex-			£2713 London, Midland and Scottish		
466 4 3 penditure for Year	135 0 0		3572 0 4 Railway 4 per cent. Preference Stock	3572 0 4	
	26,261 10 8		1143 1 0 £1200 Leeds Corporation 3% Stock ...	1143 1 0	
			£1500 Transvaal 3 per cent. Guaranteed		
Less Excess of extraordinary Ex-			1460 13 6 Stock, 1923-53	1460 13 6	
penditure over extraordinary			£1200 London and North Eastern		
— Income for Year	421 0 0		1033 11 0 Railway 3 per cent. Debenture Stock	1033 11 0	
		25,840 10 8	704 8 6 £700 Canada 3½% Stock, 1930/50 ...	704 8 6	
			1995 0 0 £2100 5 per cent. War Stock, 1929/47 ...	1995 0 0	
			1045 0 2 £1100 5% National War Bonds, 1929/47	1045 0 2	
			480 0 0 £600 4 per cent. Funding Loan, 1960/90	480 0 0	
			8987 2 2 £11,873 3½ per cent. Conversion Stock	8987 2 2	
			(Market Value £21,807 16s. 2d.)		26,296 3 3
			2593 18 10 ,, Sundry Debtors		2617 19 9
			,, Subscriptions in Arrear £886 8s. Esti-		
			500 0 0 mated to realise		500 0 0
			52 9 3 ,, Insurance paid in advance		47 7 0
			1 13 6 ,, Cash in Hand		7 0 11
			647 18 4 ,, Cash at Bank		—
£30,092 3 2		£29,468 10 11	£30,092 3 2		£29,468 10 11

RESEARCH FUND.

1925		1926	1925		1926
£ s. d.		£ s. d. £ s. d.	£ s. d.		£ s. d. £ s. d.
	To Donations:—		1185 10 0	By Salaries	1222 17 6
	Association of British Chemical Manu-		—	,, Superannuation of Staff	88 15 0
250 0 0	facturers	250 0 0	483 7 6	,, Books and Periodicals	526 11 4
10 10 0	Biochemical Society	10 10 0	130 4 9	,, Binding	128 12 9
5 5 0	Faraday Society	5 5 0		,, Printing, Stationery and Postage	42 2 4
45 0 0	Institute of Brewing	45 0 0		,, Lighting, Heating, Furniture, etc.	79 7 4
250 0 0	Institute of Chemistry	250 0 0		,, Miscellaneous	5 5 3
100 0 0	Society of Chemical Industry	100 0 0			
10 0 0	Society of Dyers and Colourists	10 10 0			
10 10 0	Society of Public Analysts	10 10 0			
—	Jones, J. P.	1 1 0			
—	,, Contribution from General Fund	1410 15 6			
		£2093 11 6			£2093 11 6

£30,092	3	2			£29,468	10	11	647	18	4	,, Cash at Bank ... ... —
£30,092	3	2			£29,468	10	11	£30,092	3	2	

RESEARCH FUND.

1925				1926			1925				1926				
£	s.	d.		£	d.	£ s. d.	£	s.	d.		£	s.	d.	£ s. d.	
14,462	4	2	To Excess of Assets over Liabilities as per last Balance Sheet	14,444	12 6					By Investments (value when acquired):					
—			*Add* Excess of Income over Expenditure for Year	27	3 9		1010	0	0	£1000 London and North Eastern Railway 4 per cent 2nd Guaranteed Stock	1010	0	0		
						14,471 16 3	1049	15	11	£1034 Gt. West. Rly. 2½% Debentures	1049	15	11		
17	11	8	*Less* Excess of Expenditure over Income for Year			—	1000	0	0	£1142 16*s.* 0*d.* New South Wales 3 per cent. Stock 1935	1000	0	0		
							1002	16	9	£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9		
							1009	18	9	£853 London, Midland and Scottish Railway 4% Debenture Stock ...	1009	18	9		
							706	6	2	£806 Victoria 3% Stock, 1929/49 ...	706	6	2		
							4267	4	10	£4498 11*s.* 0*d.* 5% War Stock, 1929/47	4267	4	10		
							3898	14	10	£5164 13*s.* 9*d.* 3½% Conversion Stock (Market Value £12,576 7*s.* 9*d.*)	3898	14	10	13,944 17 3	
							99	15	3	,, Cash at Bank ... Current Account	26	19	0		
							400	0	0	Do. ... Deposit Account	500	0	0		
														526 19 0	
£14,444	12	6				£14,471 16 3	£14,444	12	6					£14,471 16 3	

THE EDWARD FRANK HARRISON MEMORIAL TRUST

1251	6	8	To Excess of Assets over Liabilities as per last Balance Sheet	1305	14 11					By Investments (value when acquired):—					
—			*Less* Excess of Expenditure over Income for Year	84	12 2		500	0	0	£500 National War Bonds 5 per cent. 1928	500	0	0		
						1221 2 9	500	0	0	£500 National War Bonds 5 per cent. 1929	500	0	0		
							50	1	5	£61 15*s.* 8*d.* 3½ per cent. Conversion Stock (Market Value £1099 6*s.* 0*d.*)	50	1	5	1050 1 5	
54	8	3	*Add* Excess of Income over Expenditure for Year			—	55	13	6	Cash at Bank ... ... Current Account	71	1	4		
							200	0	0	Do. ... ... Deposit Account	100	0	0		
														171 1 4	
£1305	14	11				£1221 2 9	£1305	14	11					£1221 2 9	

PUBLICATIONS FUND

12	10	0	To Subscriptions received in advance ...			13 2 0				By Investments (value when acquired):—					
			,, Excess of Assets over Liabilities as per				3500	0	0	£5933 10*s.* 2*d.* 3½% Conversion Stock ...	4500	0	0		
1536	13	0	last Balance Sheet	4055	7 4		—			£2291 7*s.* 0*d.* 5% War Loan 1929/47 ...	2300	0	0		
2518	14	4	*Add* Excess of ordinary Income over ordinary Expenditure for Year	1157	15 1					(Market Value £6806 0*s.* 6*d.*)				6800 0 0	
			,, Excess of extraordinary Income over extraordinary Expenditure for year	1943	19 4		18	0	0	,, Life Composition Fee				—	
—							549	17	4	,, Cash at Bank				370 3 9	
						7157 1 9									
£4067	17	4				£7170 3 9	£4067	17	4					£7170 3 9	

SPECIAL PUBLICATIONS FUND

1925	*Liabilities.*	1926		1925	*Assets.*	1926	
£ s. d.		£ s. d	£ s. d.	£ s. d.		£ s. d	£ s. d.
	To Excess of Assets over Liabilities as per				By Investment:—		
1896 8 4	last Balance Sheet	1723 15 4	—	1600 0 0	£2115 8*s.* 10*d.* 3½% Conversion Stock ... (Market Value £1602 16*s.* 8*d.*)		1600 0 0
	Less Excess of Expenditure over In-						
172 13 0	come to 31st December, 1926	19 8 1		45 15 0	,, Sundry Debtors for Sales (Less Commission)		43 12 6
			1704 7 3	78 0 4	,, Cash at Bank ... ... Current Account	10 14 9	
					Do. ... ... Deposit Account	50 0 0	
							60 14 9
£1723 15 4			£1704 7 3	£1723 15 4			£1704 7 3

STAFF PENSIONS FUND

15 15 0	To Excess of Income over Expenditure		—		By Investment £371 17*s.* 1*d.* War Stock 5%		
	,, Excess of Assets over Liabilities as per			—	1929/47 (Market Value £375 2*s.* 1*d.*) ...		375 0 0
—	last Balance Sheet	15 15 0		15 15 0	,, Cash at Bank		15 11
	Add Excess of Income over Expenditure						
—	for year...	362 0 11					
			377 15 11				
£15 15 0			£377 15 11	£15 15 0			£377 15 11

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balances at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

23, QUEEN VICTORIA STREET, E.C. 4.
February 9th, 1927.

Approved { J. S. S. BRAME,
A. J. ALLMAND,
G. W. MONIER-WILLIAMS

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 24th, 1927.

By H. BRERETON BAKER, C.B.E., D.Sc., F.R.S.

Experiments on Molecular Association.

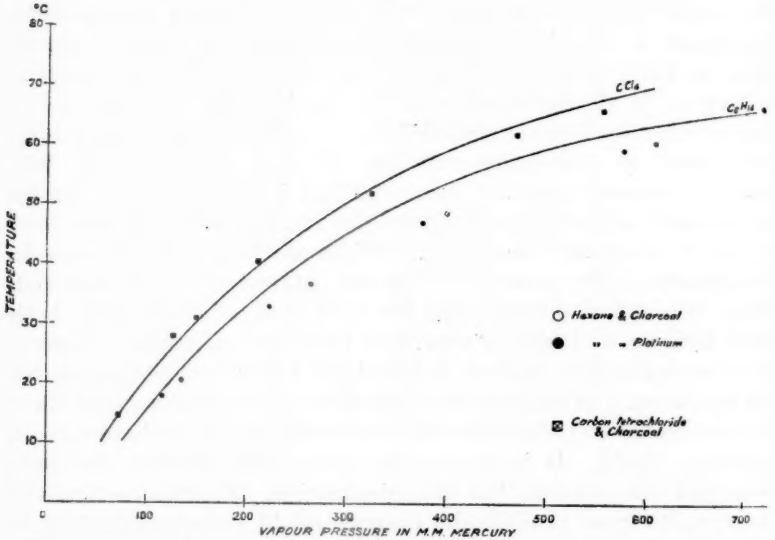
THE molecular constitution of liquids has been the subject of much investigation. It is known that in acetic acid we have molecules which have double the simple formula, and that this complex is stable even when the liquid is converted into vapour. In water, the association is even greater than this at low temperatures, but the larger molecules are less stable and can scarcely persist when the liquid is vaporised. Bromine shows some evidence of association in the vapour, but owing to experimental difficulties, little is known as to the constitution of the liquid. On the other hand, liquids such as benzene and the lower-boiling paraffins have been considered as containing only the simplest molecules. It was shown, however, some five years ago that if liquids of very diverse types were subjected to prolonged drying, the boiling points were raised to a considerable extent. This is ascribed to the increase in complexity of the molecules when the catalyst, water, is removed. Since this rise of boiling point has been shown to take place both with benzene and with hexane, two typically unassociated liquids, it is probable that, instead of associated liquids being exceptional, all liquids may be capable of association. It is supposed that there is a continual combination and dissociation of the molecules in an ordinary liquid. It is known that water can promote, not only chemical combination, but also dissociation. If water is removed as completely as possible, its absence might conceivably work in two directions: the molecular equilibrium might be reached when the molecules were much more complex owing to absence of dissociation, or, in a liquid which was normally associated, the molecules might be much less complex owing to their inability, in absence of water, to combine together. The latter state has not yet been attained; we have not been able to obtain dry liquids which boil at a lower temperature than the normal. It is true that in the very fruitful week when Prof. Smits was working with me in my laboratory, dried benzene was fractionally distilled and the first fraction which came over boiled at 80°, leaving the higher-boiling fraction (118°) behind. If instead of benzene, which is normally associated only to a small extent, we had been dealing with bromine, which is much more associated in its normal condition, it is possible that we should have been able to distil off a fraction boiling below 59°.

It was with the hope of throwing some light on this question of the equilibrium of complex and simple molecules in a liquid that a new series of experiments was undertaken, with the object of finding out if catalysts other than water had a disturbing influence. I wish to acknowledge here the invaluable help given in their performance by my assistant, Miss M. Carlton.

Two main methods of attack on the problem were chosen, the determination of the vapour pressure and the measurement of surface tension.

In the first series of experiments on vapour pressures, charcoal was used as the catalyst. Barometer tubes were made of hard

FIG. 1.



The continuous curves are the normal vapour pressure–temperature curves.

Jena glass, one end of which dipped under mercury. The upper ends were furnished with bulbs in which very pure sugar charcoal could be heated to redness while the tube was being exhausted. After admission of the liquid, the tube connecting the bulb with the pump was sealed off and the tubes were surrounded by a jacket of circulating water.

The results of these preliminary experiments left no doubt as to the influence of the presence of charcoal on the vapour pressure. With ether at 16°, the vapour pressure was 25 mm. greater than with the liquid alone. With methyl alcohol at 18°, the vapour pressure was 6 mm., and at 35° 12 mm., greater in the presence of the catalyst. With benzene, the increase with the charcoal was

2 mm. only, and this excess of vapour pressure was unaltered whether the temperature was 23° or 37°.

It was found, however, that quantitative measurements of the vapour pressures of each of the liquids showed considerable variations and a lengthy series of experiments was made using the two methods devised by Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, 32, 907, 1412). Some of the results are given in Fig. 1. These experiments again failed to give results which were concordant when the same liquid and the same catalyst were used in successive experiments. They did, however, lead to two important conclusions. We had ascribed our failure to obtain concordant results in the first series to the difficulty of obtaining the catalysts in the same condition of activity; different methods of treatment, different temperatures of treatment, and even age alone might have influenced their catalytic power.

The first fact which became clear in these preliminary experiments was that a catalyst in a liquid acts very slowly and sometimes at first even in a contrary direction to that shown in the final equilibrium. That is, in any liquid there is a balance between the large and the small molecules, for in all the liquids, ten in number, which we have examined there is evidence of some association. The presence of certain catalysts can influence the equilibrium, under different temperature conditions, in the direction of producing more complex molecules and so lowering the vapour pressure, and then, under different conditions, especially long time of contact, may produce increased dissociation and higher vapour pressure.

The second difficulty was caused by the fact that a pure liquid appears to have no constancy in its composition. For instance, pure bromine, without any catalyst, gave vapour pressures which showed considerable variations according to the history of the particular specimen. If bromine were boiled for some time and the measurement taken as soon afterwards as possible, it was found that the vapour pressure was very sensibly higher than it had been before the boiling took place. The recovery of the old vapour pressure was quite slow and many days elapsed before the effect of the boiling had disappeared.

In order to eliminate the effect of this change in the liquid alone, the next series of experiments was designed. In them the vapour pressure of the liquid was balanced against the pressure of the liquid with the catalyst, through a pressure gauge. The form of the apparatus is seen in Fig. 2.

To each of the upper ends of a U-shaped tube containing mercury was sealed a pair of bulbs, which were connected with each other by a capillary tube. Into one bulb was introduced the catalyst,

and the liquid was placed in the second of the pair. The same liquid was then introduced into one of the bulbs of the other pair, the second one being left empty. All the entrance tubes but one were sealed off. The remaining tube was connected to a Hyvac pump. The liquid in the two bulbs was allowed to boil in the evacuated space in order to get rid of dissolved air: the liquid was then frozen and thereafter the bulb containing the catalyst was suitably heated with the same object. The tube connected with the pump was now sealed off, and the apparatus allowed to stand for an hour. Finally, the capillary tube connecting the two sets of bulbs was sealed with a fine-pointed flame. On transferring the apparatus to a thermostat it was found that the mercury level was the same in both limbs of the U-tube, showing that the apparatus was in order. By cooling the bulb containing the catalyst, the liquid was distilled over from the adjoining bulb. In this way, the two lots of liquid could be treated in exactly the same way, and a direct determination could be made of the difference in vapour pressure brought about by the catalyst. The results are in the table on p. 953.

FIG. 3.

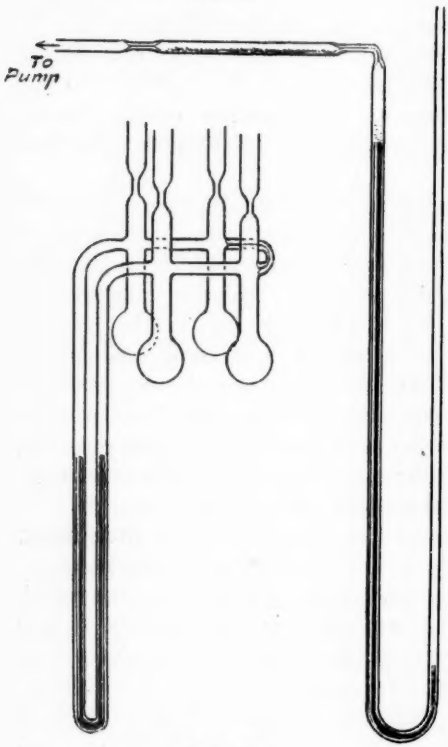


FIG. 2.

In each of the systems investigated there was an increase in the vapour pressure of the liquid in contact with the catalyst over the vapour pressure of the liquid alone. This difference increased with time up to a certain point and then became constant. The effect of the increase of vapour pressure produced by a catalyst was always seen with this apparatus, for, on standing, the liquid evaporated away from the catalyst and condensed in another part of the apparatus, although the whole was kept at a constant temperature in a thermostat.

The effects of heating and of cooling on this difference of vapour pressure were investigated and it was found that heating increased the difference and cooling diminished it. On standing, however, the original value of the difference was restored, although in some cases the time needed was some weeks.

Acetic acid and charcoal.		Acetic acid and platinum black.		Acetic acid and thoria.	
Time.	Diff. in mm. Hg.	Time.	Diff. in mm. Hg.	Time.	Diff. in mm. Hg.
Day of sealing	2·15	Day of sealing	0·3	Day of sealing	0·4
2 Days later ...	1·5	1 Day later ...	0·25	3 Weeks later...	0·25
After heating at 80° for 4 hrs....	2·95	After heating at 80° for 4 hrs....	0·5	3 Weeks later...	1·27
6 Days later ...	2·0	1 Day later.....	0·75	Heated at 90° for 4 hrs.	1·32
After keeping at 15° for 24 hrs.	2·05	6 Days later ...	0·8		
2 Days later ...	2·4	After cooling at 15° for 1 day	1·05		
5 Months later	1·9	3 Days later ...	1·6		
		After heating at 90° for 4 hrs.	1·75		
		5 Months later	2·2		

Benzene and nickel. Diff. in mm. Hg.	Methyl alcohol and charcoal. Diff. in mm. Hg.	Ether and charcoal. Diff. in mm. Hg.
3·4	5·5	40·0
3·3	6·3	41·3
3·3	6·2	41·2
3·5	6·5	39·2
3·1	6·1	40·2

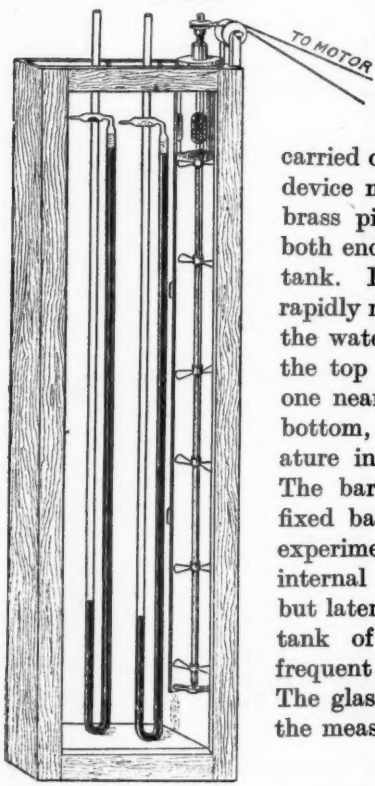
Bromine and charcoal.

Time.	Diff. in mm. H_2SO_4 satd. with bromine.	Time.	Diff. in mm. H_2SO_4 satd. with bromine.
—	38·5	Interval of 2 days ...	95·2
Interval of 2 days ...	50·9	Interval of 14 days ...	125·1
Interval of 1 day	51·7	Interval of 16 days ...	133·75
Interval of 1 day	52·8	Interval of 3 days ...	142·3
Interval of 6 days ...	85·2		

In order to investigate the effect of heating on the vapour pressure of the liquid alone as well as in presence of catalysts, a return was made to the barometer tube method, with greatly improved apparatus (Fig. 3). The tube was U-shaped and made of Jena glass. The upper end of one limb was bent into a horizontal position, and by drawing it out to a capillary a bulb was formed, about 2 inches in length, to hold the catalyst. The liquid was introduced into the main barometer tube, and the catalyst into its bulb. The tube was then exhausted through the capillary and, after the liquid had been allowed to boil to expel dissolved air, the part of the vertical tube containing it was frozen and the catalyst was heated. As it was found difficult to obtain

charcoal in the same state of activity in successive experiments, it was necessary to give this substance the same heat treatment. This was accomplished by slipping over the horizontal bulb a small electric furnace which maintained the charcoal at 450° for 1½ hours, the pump being kept running during the whole period. The capillary tube was then sealed, and the tube transferred to a large thermostat (Fig. 4). This was 1 sq. ft. in section and 3 ft. 6 in. in height. It was built of heavy teak, with thick plate-glass windows on opposite sides. It was filled with water and the stirring was carried out most effectively by an ingenious device made by Mr. W. J. Colebrook. A brass pipe, 5 inches in diameter, open at both ends, extends the whole height of the tank. In it is a screw propeller which, rapidly rotated by an electric motor, pumps the water continually from the bottom to the top of the tank. Two thermometers, one near the top and the other near the bottom, indicate the constancy of temperature in the different parts of the tank. The barometer tubes were clamped to a fixed bar inside the tank. In the earlier experiments, heating was effected by an internal coil carrying superheated steam, but later this was carried on in a separate tank of galvanised iron, owing to the frequent fracture of the glass windows. The glass-fronted thermostat was kept for the measurements alone.

FIG. 4.



Acetic Acid.

Catalyst.	Before heating.	Heated at 80° for 24 hrs., then cooled to 20°.	One week after heating at 20°.
None.	Normal.	+2 mm.	Normal.
Charcoal.	+1·8 mm. After an interval of 6 weeks, +6·0 mm.	+2·3 mm	+6·8 mm.
Thoria.	+0·65 mm. After an interval of 6 weeks, +7·3 mm.	+1·5 mm.	+7·3 mm.
Platinum.	+2·72 mm. After an interval of 6 weeks, −1·2 mm.	−3·8 mm.	+1·1 mm.

Water.

Catalyst.	Before heating.	Heated at 80° for 48 hrs., then cooled to 20°.	Two weeks after, at 20°.
None.	Normal.	Normal.	Normal.
Charcoal.	+2·5 mm.	+4·3 mm. 1 Day later, +0·75 mm.	+2·5 mm.
Thoria.	+2·4 mm.	+4·0 mm. 1 Day later, +1·2 mm.	+0·9 mm.
Platinum.	+1 mm.	+3·2 mm. 1 Day later, +0·6 mm.	+0·5 mm.

Measurements of the vapour pressure of water in the presence of the catalysts charcoal, platinum, and thoria show that in each instance heating has the same ultimate effect, but the interval between the actual heating and the appearance of the effect of the heating varies with the different catalysts. With thoria and platinum, heating at 80° for 24 hours produces an increase in vapour pressure, at the ordinary temperature, but if the time of heating be prolonged to 48 hours the vapour pressure within 24 hours of the heating shows a decrease from the constant value, this decrease disappearing if the tubes be allowed to stand for a few days at room temperature.

The charcoal and water, when heated at 80° for 24 hours, shows an increase in vapour pressure, if the readings be made within 24 hours of the heating; but two days after the heating the value of the vapour pressure diminishes and becomes less than before heating. This low value slowly changes back to the constant value when the barometer tubes containing the water and charcoal are allowed to stand at the ordinary temperature for a few days.

With acetic acid, charcoal as catalyst produces a decrease after 24 hours' heating; after 72 hours' heating, there is a decrease which temporarily increases for a day or two, the normal value finally returning. Thoria causes a decrease in vapour pressure when heated with acetic acid, the amount of the decrease being greatest a day or two after the heating has taken place. With platinum, a diminution in vapour pressure is caused by heating, the normal value returning after a short while.

Surface Tension Measurements.

The vapour pressure determinations having shown that the presence of catalysts produces a change in liquids, experiments were undertaken to find the molecular weights of some liquids by the method of Ramsay and Shields. Although the absolute accuracy of this method has been disputed, the differences we have found between the molecular weights of liquids alone and in the presence

of catalysts are so marked that any small deviations from the true values are probably unimportant.

The determinations of the diameters of the capillary tubes were made with a microscope, kindly lent by Professor Fowler, which reads directly to the 1/1000th of a millimetre. These capillaries were sealed to glass sinkers and cleaned with a mixture of nitric and chromic acids. The containing tubes were made of special resistant glass, the formula of which was worked out by myself and the late Mr. H. J. Powell, of the Whitefriars Glass Works. The liquids were shown to have taken up no weighable amounts either from the glass or from the catalyst even after a year's contact.

The measurements were taken in a large thermostat provided with an electrically driven stirrer. Half an hour before the heights of the liquids in the capillaries were measured, the tubes were taken out and tilted to see that the liquids ran freely in the capillaries. There was always a danger that the finely powdered catalyst might block the minute opening at the bottom of the capillary. The catalysts and the liquids used were from the same preparations as those which were used in the vapour pressure experiments.

The study of surface tension was directed chiefly to the effect of three catalysts—pure charcoal, platinum black, and oxide of thorium—on the three liquids water, acetic acid, and bromine.

In all cases, comparative tubes were used containing the liquid alone, without the presence of any catalyst, so that a direct estimation of the effect of the catalyst could be made under various conditions of temperature, etc.

It has been found that the catalyst does not seem to produce its maximum effect on the complexity of the molecules at once. This is seen by the following table: the temperature interval was about 20°, the higher temperature being 40°.

Acetic Acid and Charcoal.

Time.	Mol. wt.
After 1 day	1·541 × 60
„ 2 days	1·952 × 60
„ 3 weeks	2·525 × 60
„ 12 months	2·492 × 60

Acetic Acid alone.

Time.	Mol. wt.
After 1 day	1·546 × 60
„ 2 days	1·568 × 60
„ 3 weeks	2·097 × 60
„ 9 months	2·097 × 60

Acetic Acid and Platinum Black.

Time.	Mol. wt.
After 2 weeks	2·40 × 60
„ 3 months	2·273 × 60
„ 8 months	2·976 × 60

Acetic Acid and Thoria.

Time.	Mol. wt.
After 1 day	2·538 × 60

The table for acetic acid alone shows that the acid does not reach its normal value in 2 days after filling. This points to the conclusion that in the process of filling the tube, which involves the

boiling of the liquid for some time to get rid of air, dissociation of the molecules of liquid takes place, and that in 3 weeks the normal molecular weight is restored. With charcoal the same phenomenon is observed, but the molecular weight is greater by 24. With platinum black, the molecular weight is greater by 52, whilst with thoria the increase in molecular weight due to the catalyst is 29.

A similar effect is seen with water and the same catalysts.

Water and Platinum.		Water and Thoria.	
Time.	Mol. wt.	Time.	Mol. wt.
Day of filling	3·352 × 18	3 Weeks after filling ...	3·125 × 18
After 6 months	4·442 × 18	5 Weeks after filling ...	3·612 × 18
Heated at 40° for 16 hrs.	3·948 × 18	9 Weeks after filling ...	3·866 × 18
1 Week later	3·713 × 18		
2 Weeks later	3·047 × 18		
1 Day later	2·915 × 18		

Ramsay and Shields' value for this temperature interval is 3·259 × 18.

This method, as used, appears to have a disadvantage because the heating, even to only 40°, seems to disturb the equilibrium and this is not restored at once on cooling to the ordinary temperature. It was therefore decided to make a study of the effect of temperature on the constitution of these liquids in presence and in absence of catalysts. It must be pointed out that, after heating or cooling, the liquids were allowed to stand at the ordinary temperature for the time specified, so that the effects shown are those not measured at the high or low temperature, but through the usual interval 17—40°.

Acetic Acid.

Catalyst.	Before heating.	After heating at 80° for 2 hrs.	After heating at 80° for 48 hrs.	After 24 hrs. at the ordinary temperature.
None	2·168 × 60	2·32 × 60	1·97 × 60	1·666 × 60
Platinum black	1·872 × 60	2·527 × 60	1·782 × 60	1·586 × 60
Charcoal	2·492 × 60	2·552 × 60	1·690 × 60	2·490 × 60
Thoria	1·992 × 60	2·538 × 60	2·218 × 60	2·452 × 60

Attention may be directed, not only to the effect of the catalysts on the complexity of the molecules of the different liquids, but also to the different effects of heating for various lengths of time. Except in the cases of bromine alone and of charcoal in acetic acid, heating for only a short period seems to increase the molecular complexity, whilst heating for a long period decreases it, as would be expected. The recovery to normal is slow, but even after 3 days' standing at the ordinary temperature the molecular weight is often considerably above or below that at the beginning of the experiments.

The agreement between the vapour-pressure and the surface-tension results is not quantitative. This could not be expected, since, by the surface tension method the *average* complexity of the molecules is estimated, whilst the vapour pressure measured will be, very largely at all events, that of the smaller molecules present.

The view of the constitution of liquids which is indicated by these experiments is that all liquids may be regarded as analogous to a dissociable gas such as nitrogen tetroxide. At low temperatures the heavy molecules are more numerous; at higher temperatures the lighter ones predominate, and dissociation and combination are probably both increasing. Liquids differ, however, in this respect, that dissociation and association are much slower in liquids than in gases. Equilibrium in liquids may be profoundly disturbed by even a comparatively slight change of temperature, and complete recovery of the normal condition may be a question of weeks or even months.

The effect of the presence of a solid catalyst is, as would be expected, produced much more slowly in a liquid than in a gas, and it is not easy to understand how the catalyst comes to exert its special influence. All one can say at present is that this influence is exerted in the case of all the liquids on which experiments have been made.

OBITUARY NOTICE.

JOSEPH JOHN ACWORTH.

BORN 1853; DIED JANUARY 3RD, 1927.

DR. ACWORTH was born at Rochester in 1853 and died on January 3, 1927, aged 73. He was elected a Fellow of this Society on March 4, 1875, so that he had more than completed his Jubilee of fellowship. He was admitted a Fellow of the Institute of Chemistry in 1878, that is, the year after the Institute was founded.

Acworth was from his boyhood interested in experimental science, and after working in the Chemical Laboratories of the Royal College of Chemistry at South Kensington, he communicated a paper to this Society "On the Action of Nitric Acid upon Copper, Mercury, etc., and on the Influence of the Presence of Metallic Nitrates," which was published in the *Journal* for 1875. He appears to have continued working at this subject at the London Institution with Prof. H. E. Armstrong, and a paper in their joint names was published in the *Journal* two years later, "Researches on the Reduction of Nitric Acid and the Oxides of Nitrogen. Part I. On the Gases evolved by the Action of Metals on Nitric Acid." After this he passed to what proved to be his life work, namely, the manufacture of photographic sensitive materials. It was in quite the early days of the gelatine dry plate industry that he spent a few years in the laboratories of the Britannia Dry Plate Company (now the Ilford Company), and leaving there went to the University of Erlangen to work for the Ph.D. degree in Wiedemann's laboratories. His thesis was presented in May, 1890, and printed (*Ann. Phys. Chem.*, 1891, pp. 371—406) in 1891, "On the Relation between Absorption and Sensitiveness of Sensitised Plates," chiefly plates that had been sensitised for colour by dyes. A translation of the essential parts of this paper appeared in the *Photographic Quarterly* for April, 1891. Acworth was back again in England in 1890 (aged 37), and built a factory at Cricklewood for the manufacture of gelatine dry plates, and in March, 1892, the "Imperial" plates were advertised for sale. These works under his personal guidance, both technically and commercially, were probably the most prosperous of any in the country. Ill health led him to dispose of his interests in the company about the year 1917 (*Brit. Journ. Phot.*).

Eastman, in 1889, introduced commercially his transparent rollable film, the base being nitrocellulose. In 1890, Acworth was

granted a patent for a film base of gelatine rendered waterproof by passing it through a solution of nitrocellulose. This method does not appear to have been followed up. From 1892 to 1896, inclusive, he made four communications to the Royal Photographic Society and one to the Camera Club, which will be found in the respective Journals. In his technical work, he was very capably assisted by his wife, who, as Miss Marion Whiteford Stevenson, had taken the Associateship course at the Royal College of Science and received her diploma (A.R.C.Sc.) in physics in 1893. She was the third woman to earn the Associateship, and the first in physics.

Acworth was of a very kindly and genial nature, and he was in no sense "spoiled" by either his prosperity or his afflictions. He suffered for very many years from asthma and other troubles apparently associated with it. This may have tended to increase his inborn nervous and retiring disposition. Those who heard him on the few occasions when he spoke in public would hardly realise how distressing it was to him to do so, for he had the necessary strength of will and power of perseverance to succeed. C. J.